Supporting information

Iron-Cobalt-catalyzed Heterotrimerization of Alkynes and Nitriles to Polyfunctional Pyridines

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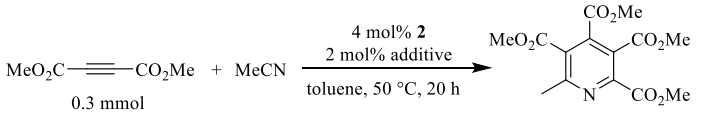
1. General information

All reactions were performed in flame-dried glassware using standard Schlenk techniques or in a glovebox under nitrogen atmosphere. Toluene and acetonitrile were dried and degassed by Solvent Purification Systems (Innovative Technology). All reagents were purchased from commercial suppliers, unless specified otherwise, or prepared as described in the literature. The Cp*Co(1,2-$Ph_2PC_6H_4NH$) (**2**)[1] and [Cp*Fe$(NCMe)_3$][PF_6] (**1**)[2] were prepared according to published procedures. NMR spectra were recorded on Bruker 500 (500 MHz for ^1H, 126 MHz for ^{13}C) spectrometers. Chemical shifts for ^1H and ^{13}C spectra were referenced to residual solvent resonances and are reported relative to tetramethylsilane. GC-MS spectra were obtained on a Shimadzu GCMS-QP2010 SE spectrometer. High resolution mass spectra (MS) were obtained using a LC/MSD TOF spectrometer system with electrospray ionization (ESI). UV-vis absorption spectra were recorded with an Agilent Cary 60 spectrophotometer. Steady-state emission spectra were recorded using a Shimadzu RF-6000 spectrofluorimeter. Crystallographic data were collected using a Rigaku Oxford Diffraction XtaLAB Synergy diffractometer equipped with a HyPix-6000HE area detector at 173 K using Mo Kα (λ = 0.71073 Å) or Cu Kα (λ = 1.54184 Å) from PhotonJet micro-focus X-ray Source. FT-IR spectra were recorded on a PerkinElmer FT-IR Spectrometer Spectrum Two (the range: from 4000 to 450 cm^{-1}). Melting point were recorded on X-5A Micro Melting Point Tester.

2. Experimental procedures

Table S1. Screening of catalysts



entry	additive	yield[a]/%
1	none	N.D.[b]
2	none	28
3	**1**	92
4	**1**	N.D.[c]
5	$FeCl_2$	32
6	$FeCl_3$	N.D.
7	$Fe(OTf)_3$	N.D.

[a] Conditions: Determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal standard. [b] Without MeCN, give hexamethyl benzene-1,2,3,4,5,6-hexacarboxylate as product in 90% yield. [c] Without **2**.

Characterization of hexamethyl benzene-1,2,3,4,5,6-hexacarboxylate: ^1H NMR (500 MHz, $CDCl_3$) δ 3.84 (s, 18H). MS (EI): m/z calcd. for $C_{18}H_{18}O_{12}$: 426.08 GC-MS: m/z 426.10. ^1H data agrees with reported data.[3]

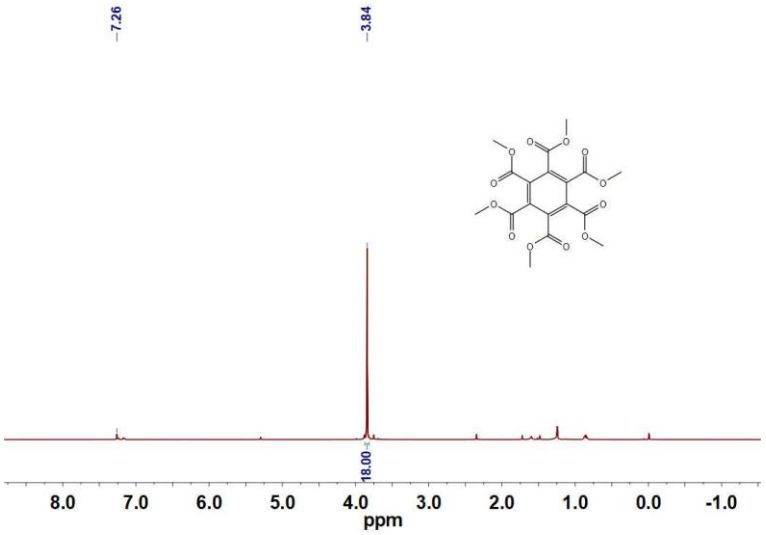


Figure S1. ^{1}H NMR spectrum of hexamethyl benzene-1,2,3,4,5,6-hexacarboxylate in $CDCl_3$

General procedures for the cycloaddition of alkynes and nitriles

[Cp*Fe(NCMe)$_3$][PF$_6$] (2.8 mg, 0.006 mmol), Cp*Co(1,2-Ph$_2$PC$_6$H$_4$NH) (5.6 mg, 0.012 mmol) and nitriles (0.9 mmol) were mixed in 2 mL toluene in a flame-dried glassware in a glove box. The alkyne substrate (0.3 mmol) was added. The mixture was stirred at 50 °C for 20 h. The reaction progress was monitored by GLC. After the reaction was complete, the solvent was evaporated *under vacuum*. The products was isolated by wash the residue through column chromatography (petroleum ether: EtOAc = 10:1).

Photophysical properties of 6h and 6i

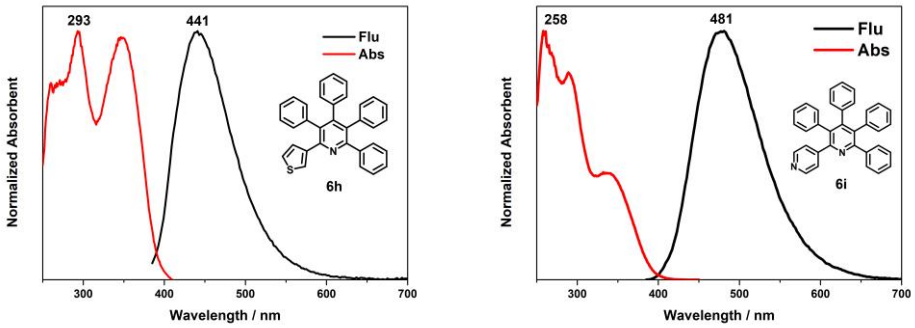


Figure S2. UV-vis absorption (red line) and fluorescence (black line) spectra of **6h** (10^{-5} M) and **6i** (10^{-5} M) in DCM with λ_{ex} = 365 nm.

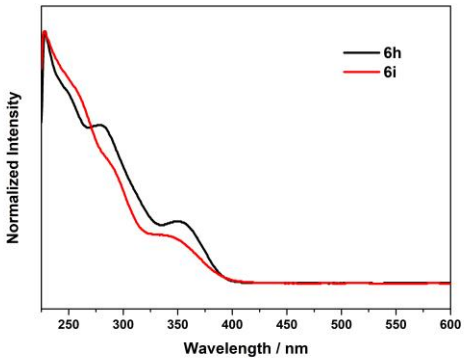


Figure S3. UV-vis absorption spectra of **6h** (10^{-5} M) and **6i** (10^{-5} M) in DCM.

ESI-MS spectrum of Int1

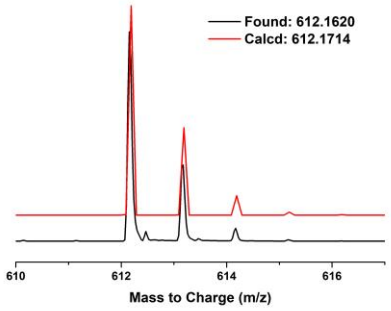


Figure S4. ESI-MS spectroscopic analysis for the reaction solution of **2** with dimethyl but-2-ynedioate *Results:* calcd for $C_{34}H_{36}CoNO_4P$, 612.1714; found, 612.1620.

FI-IR spectra of MeCN and 1 in CH_2Cl_2

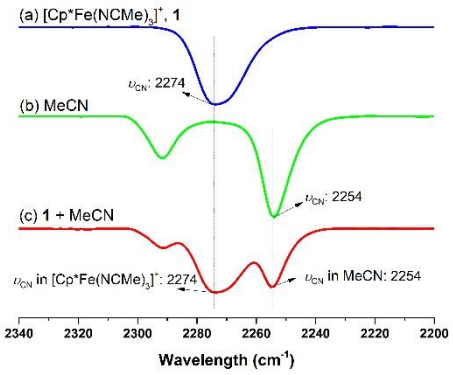


Figure S5. FI-IR spectra of (a) complex $[Cp^*Fe(NCMe)_3]^+$ (**1**), (b) pure MeCN and (c) **1** with MeCN in CH_2Cl_2.

[Cp*Fe(NCPh)$_3$]$^+$

Treatment of **1** in CH_2Cl_2 with PhCN (5 equiv) caused the purple solution to immediately turn brown. The replacement of the MeCN ligand in **1** by PhCN was suggested by the appearance of $\nu_{C\equiv N}$ band at 2254 cm^{-1} for free MeCN in the IR spectrum. The reaction solution was layered with hexane and stored at -30 oC for 24 hours, providing single crystals suitable for X-ray diffraction. Crystallographically analysis confirmed the solid-sate structure of [Cp*Fe(NCPh)$_3$]PF$_6$.

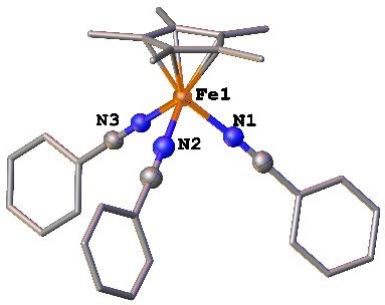


Figure S6. Structures of [Cp*Fe(NCPh)$_3$]$^+$ with 50% probability thermal ellipsoids. For clarity, hydrogen atoms and counteranions are omitted. Selected bond distances (Å): for Fe−N (avg.) 1.923, N−C (avg.) 1.145.

FI-IR spectra of PhCN and [Cp*Fe(NCPh)$_3$]$^+$ in CH_2Cl_2

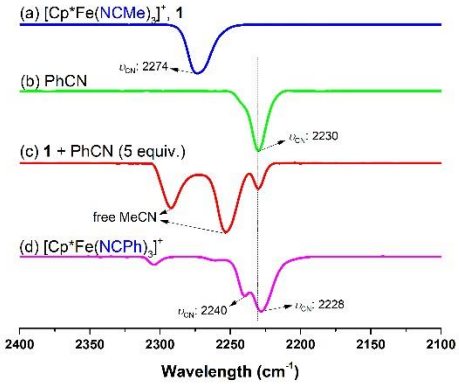
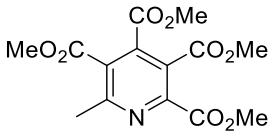


Figure S7. FI-IR spectra (CH_2Cl_2 solution) of (a) [Cp*Fe(NCMe)$_3$]$^+$ (**1**), (b) pure MeCN, (c) **1** + MeCN, and (d) [Cp*Fe(NCPh)$_3$]PF$_6$.

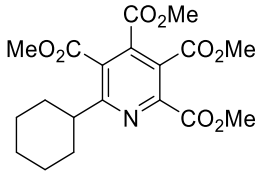
3. Characterizations

Tetramethyl 6-methylpyridine-2,3,4,5-tetracarboxylate (5a)[4]



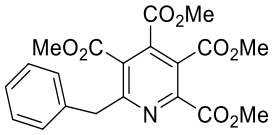
White solid, 44 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.96 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.25, 165.69, 164.69, 164.58, 158.81, 147.88, 139.15, 128.98, 126.24, 53.61, 53.37, 53.29, 23.41. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1743 cm^{-1}, ν_{C-O-C} 1267, 1263 cm^{-1}. HRMS (ESI) Calcd for $C_{14}H_{15}NO_8$ [M+H$^+$]: 326.0876; Found: 326.0850. GC-MS: 325.05.

Tetramethyl 6-cyclohexylpyridine-2,3,4,5-tetracarboxylate (5b)



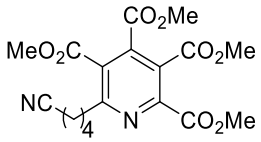
White solid, 45 mg, 76% yield. M.p.: 107-109 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (dd, J = 24.7, 14.5 Hz, 12H), 2.85 (s, 1H), 1.93 – 1.68 (m, 7H), 1.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.71, 165.95, 165.88, 165.17, 165.00, 148.55, 138.69, 128.40, 125.47, 77.41, 77.16, 76.91, 53.59, 53.38, 53.34, 53.25, 44.21, 32.11, 26.3, 25.73. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1743 cm^{-1}, ν_{C-O-C} 1267, 1263 cm^{-1}. HRMS (ESI) Calcd for $C_{19}H_{23}NO_8$ [M+H$^+$]: 394.1502; Found: 394.1497. GC-MS: 393.10.

Tetramethyl 6-benzylpyridine-2,3,4,5-tetracarboxylate (5c)



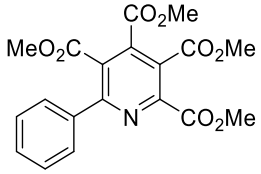
White solid, 47 mg, 61% yield. M.p.: 89-91 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.03 (m, 5H), 4.34 (s, 2H), 3.91 (s, 3H), 3.84 (s, 3H), 3.78 (s, 3H), 3.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.90, 165.64, 164.65, 164.59, 160.80, 148.01, 139.72, 137.33, 129.17, 129.13, 128.53, 126.85, 126.55, 53.55, 53.38, 53.04, 42.33. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1743 cm^{-1}, ν_{C-O-C} 1267, 1265 cm^{-1}. HRMS (ESI) Calcd for $C_{20}H_{19}NO_8$ [M+H$^+$]: 402.1189; Found: 402.1187. GC-MS: 401.05.

Tetramethyl 6-(4-cyanobutyl)pyridine-2,3,4,5-tetracarboxylate (5d)



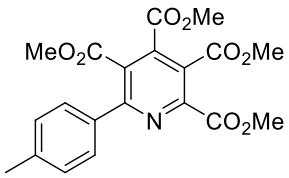
Orange oil, 47 mg, 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.98 (s, 3H), 3.93 (s, 4H), 3.92 (s, 2H), 3.90 (s, 3H), 2.99 (t, J = 7.6 Hz, 2H), 2.39 (t, J = 7.1 Hz, 2H), 2.01 – 1.86 (m, 2H), 1.79 – 1.67 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.22, 165.65, 164.73, 164.68, 161.14, 148.40, 139.48, 128.85, 126.35, 119.51, 77.41, 77.16, 76.91, 53.69, 53.62, 53.48, 53.46, 35.13, 28.13, 25.01, 17.04. MS (EI) m/z calcd. for $C_{18}H_{20}N_2O_8$: 392.12. GC-MS: m/z 392.05.

Tetramethyl 6-phenylpyridine-2,3,4,5-tetracarboxylate (5e) [5]



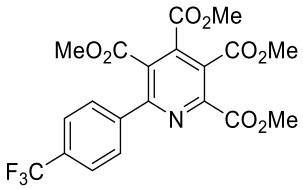
White solid, 49 mg, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.45 (d, J = 4.9 Hz, 3H), 4.03 – 3.90 (m, 9H), 3.69 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.81, 165.69, 164.75, 164.71, 158.71, 148.41, 140.23, 137.55, 130.15, 128.78, 128.72, 126.26, 53.76, 53.61, 53.51, 53.21. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1746 cm^{-1}, $\nu_{C\text{-}O\text{-}C}$ 1267, 1264 cm^{-1}. HRMS (ESI) Calcd for $C_{19}H_{17}NO_8$ [M+H$^+$]: 388.1032; Found: 388.1025. GC-MS: 387.05. Crystal was obtained by slow evaporation of the CH_2Cl_2/hexane at room temperature.

Tetramethyl 6-(p-tolyl)pyridine-2,3,4,5-tetracarboxylate (5f) [6]



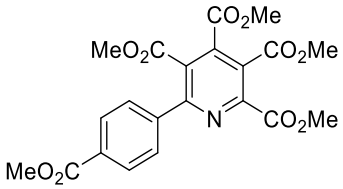
White solid, 39 mg, 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 7.3 Hz, 2H), 3.99 (s, 3H), 3.95 (s, 3H), 3.93 (s, 3H), 3.73 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.89, 165.65, 164.75, 164.70, 158.59, 148.32, 140.35, 140.13, 134.61, 129.43, 128.57, 128.34, 125.73, 53.62, 53.47, 53.38, 53.11, 21.41. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1745 cm^{-1}, $\nu_{C\text{-}O\text{-}C}$ 1267, 1264 cm^{-1}. HRMS (ESI) Calcd for $C_{20}H_{19}NO_8$ [M+H$^+$]: 402.1189; Found: 402.1177. GC-MS: 401.05.

Tetramethyl 6-(4-(trifluoromethyl)phenyl)pyridine-2,3,4,5-tetracarboxylate (5g)



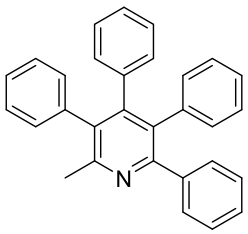
White solid, 61 mg, 89% yield. M.p.: 134-136 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 4H), 4.10 – 3.85 (m, 9H), 3.72 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.21, 165.32, 164.35, 164.31, 157.02, 148.45, 140.82, 140.27, 131.91 (q, J_{CF} = 32.7 Hz), 129.09, 128.00 (q, J_{CF} = 268.4 Hz), 125.63 (q, J_{CF} = 3.7 Hz), 122.74, 53.75, 53.58, 53.48, 53.28, 29.69. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.87. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1746 cm^{-1}, $\nu_{C\text{-}O\text{-}C}$ 1267, 1263 cm^{-1}. HRMS (ESI) Calcd for $C_{20}H_{16}F_3NO_8$ [M+H$^+$]: 456.0906; Found: 456.0908. GC-MS: 455.10.

Tetramethyl 6-(4-(methoxycarbonyl)phenyl)pyridine-2,3,4,5-tetracarboxylate (5h)



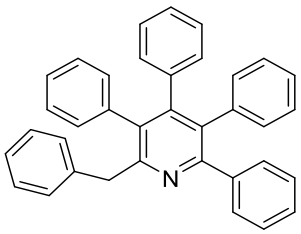
White solid, 61 mg, 92% yield. M.p.: 150-152 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 3.99 (s, 4H), 3.95 (s, 3H), 3.93 (s, 2H), 3.92 (s, 2H), 3.68 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.53, 166.40, 165.45, 164.51, 164.48, 157.59, 148.53, 141.66, 140.37, 131.48, 129.93, 129.01, 128.80, 126.90, 77.41, 77.16, 76.91, 53.81, 53.67, 53.55, 53.33, 52.44. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1745 cm^{-1}, $\nu_{C\text{-}O\text{-}C}$ 1267, 1263 cm^{-1}. HRMS (ESI) Calcd for $C_{21}H_{19}NO_{10}$ [M+H$^+$]: 446.1087; Found: 446.1091. GC-MS: 445.15.

2-methyl-3,4,5,6-tetraphenylpyridine (6a) [7]



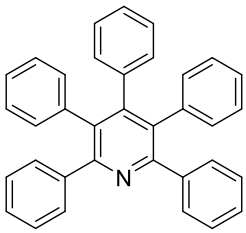
White solid, 41 mg, 69% yield.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.23 – 7.13 (m, 6H), 7.09 – 7.04 (m, 2H), 6.99 – 6.94 (m, 3H), 6.92 – 6.88 (m, 3H), 6.88 – 6.83 (m, 2H), 6.77 – 6.71 (m, 2H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.19, 155.34, 149.30, 140.99, 138.86, 138.44, 138.16, 134.73, 132.63, 131.40, 130.27, 130.08, 129.97, 127.84, 127.64, 127.33, 127.23, 126.92, 126.63, 126.11, 77.30, 77.04, 76.79, 24.31. HRMS (ESI) Calcd for $C_{30}H_{23}N$ [M+H$^+$]: 398.1909; Found: 398.1908. GC-MS: 397.10.

2-benzyl-3,4,5,6-tetraphenylpyridine (6b) [8]



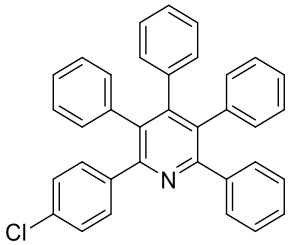
White solid, 38 mg, 52% yield. M.p.: 153-155 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 2H), 7.23 – 7.17 (m, 5H), 7.15 (dd, *J* = 6.1, 2.5 Hz, 4H), 7.11 – 7.06 (m, 2H), 7.01 – 6.90 (m, 5H), 6.82-6.87 (m, 5H), 6.74 – 6.65 (m, 2H), 4.15 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.16, 140.96, 138.15, 131.34, 130.60, 130.18, 129.19, 127.96, 127.59, 127.32, 126.77, 126.10, 125.83, 42.47. HRMS (ESI) Calcd for $C_{36}H_{27}N$ [M+H$^+$]: 473.2222; Found: 474.2225. GC-MS: 474.23.

2,3,4,5,6-pentaphenylpyridine (6c) [9]



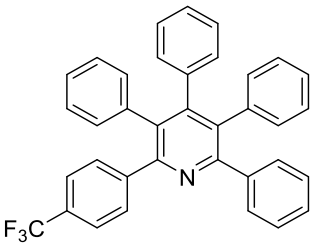
White solid, 44 mg, 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 6.5, 2.9 Hz, 4H), 7.23 – 7.13 (m, 6H), 7.05 – 6.96 (m, 6H), 6.92 (m, 7H), 6.78 (dd, *J* = 6.4, 2.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.42, 150.25, 140.89, 138.45, 138.16, 133.69, 131.32, 130.43, 130.22, 127.50, 127.38, 127.31, 126.96, 126.25, 126.18. HRMS (ESI) Calcd for $C_{35}H_{25}N$ [M+H$^+$]: 460.2065; Found: 460.2064. GC-MS: 459.90.

2-(4-chlorophenyl)-3,4,5,6-tetraphenylpyridine (6e)



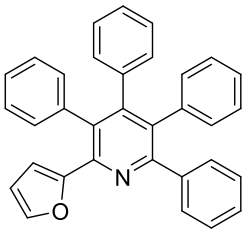
White solid, 46 mg, 62% yield. M.p.: 240-242 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.38 – 7.34 (m, 2H), 7.21 – 7.18 (m, 3H), 7.17 – 7.14 (m, 2H), 7.06 – 6.99 (m, 6H), 6.96 – 6.89 (m, 7H), 6.77 (dd, *J* = 6.6, 3.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.74, 155.21, 150.61, 140.92, 139.53, 138.47, 138.36, 138.15, 134.13, 133.80, 133.64, 131.74, 131.43, 131.38, 130.55, 130.32, 127.89, 127.77, 127.69, 127.58, 127.16, 126.65, 126.65, 126.41. HRMS (ESI) Calcd for $C_{35}H_{24}ClN$ [M+H$^+$]: 494.1676; Found: 494.1662. GC-MS: 493.70.

2,3,4,5-tetraphenyl-6-(4-(trifluoromethyl)phenyl)pyridine (6f)



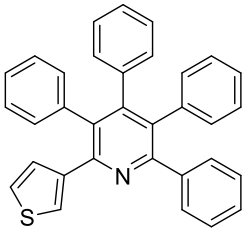
Yellow solid, 48 mg, 61% yield. M.p.: 192-194 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 4.8 Hz, 1H), 7.20 (s, 3H), 7.03 (d, *J* = 10.3 Hz, 6H), 6.93 (d, *J* = 16.1 Hz, 7H), 6.84 (s, 1H), 6.78 (d, *J* = 3.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 154.86, 150.54, 144.45, 140.63, 138.16, 137.88, 137.82, 134.38, 133.94, 131.24, 131.21, 130.51, 130.38, 130.15, 129.24 (q, J_{CF} = 32.3 Hz), 128.91 (q, J_{CF} = 294.84 Hz), 127.66, 127.59, 127.53, 127.47, 127.07, 126.6, 126.58, 126.43, 126.36, 125.32, 125.19, 124.48 (q, J_{CF} = 3.7 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.51. HRMS (ESI) Calcd for $C_{36}H_{25}F_3N$ [M+H$^+$]: 528.1939; Found: 528.2008.

2-(furan-2-yl)-3,4,5,6-tetraphenylpyridine (6g)



White solid, 40 mg, 59% yield. M.p.: 203-205 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 3H), 7.22 – 7.18 (m, 6H), 7.11 – 7.07 (m, 2H), 7.00 – 6.96 (m, 3H), 6.93 – 6.89 (m, 3H), 6.88 (dd, *J* = 6.5, 3.1 Hz, 2H), 6.76 (dd, *J* = 6.5, 3.1 Hz, 2H), 6.23 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.66 (d, *J* = 3.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.93, 152.75, 150.77, 146.29, 143.17, 140.89, 138.50, 138.42, 137.96, 133.58, 132.41, 131.42, 130.56, 130.37, 128.13, 127.76, 127.59, 127.51 127.17, 127.08, 126.40, 126.35, 112.51, 111.27. HRMS (ESI) Calcd for $C_{33}H_{23}NO$ [M+H$^+$]: 450.1858; Found: 450.1850. GC-MS: 448.90. Crystal was obtained by slow evaporation of the CH_2Cl_2/hexane at room temperature.

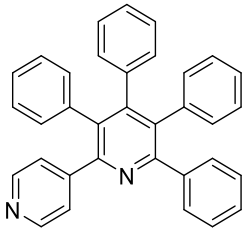
2,3,4,5-tetraphenyl-6-(thiophen-3-yl)pyridine (6h)



White solid, 32 mg, 46% yield. M.p.: 204-206 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.23 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.20 (dt, *J* = 4.5, 2.3 Hz, 3H), 7.16 –

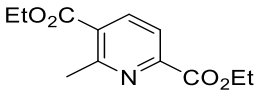
7.12 (m, 3H), 7.09 (dt, *J* = 3.1, 2.3 Hz, 2H), 7.05 – 6.98 (m, 5H), 6.94 – 6.88 (m, 5H), 6.78 (d, *J* = 3.6 Hz, 1H), 6.76 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.21, 150.89, 150.47, 41.99, 140.88, 138.78, 138.45, 138.08, 133.27, 133.00, 131.30, 130.86, 130.33, 130.23, 129.49, 127.90, 127.49, 127.39, 127.37, 126.94, 126.83, 126.30, 126.23, 126.15, 123.71. HRMS (ESI) Calcd for $C_{33}H_{23}NS$ [M+H$^+$]: 466.1629; Found: 466.1621. GC-MS: 465.70. Crystal was obtained by slow evaporation of the CH_2Cl_2/hexane at room temperature.

3,4,5,6-tetraphenyl-2,4'-bipyridine (6i) [10]



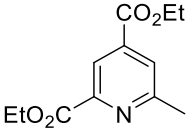
White solid, 42 mg, 63% yield. ^{1}H NMR (500 MHz, CDCl3) δ 8.43 (d, *J* = 5.6 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.31 (dd, *J* = 4.6, 1.5 Hz, 2H), 7.21 – 7.16 (m, 3H), 7.04 (tdd, *J* = 6.9, 4.9, 2.3 Hz, 6H), 6.95 – 6.89 (m, 7H), 6.77 (dd, *J* = 6.5, 3.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.09, 153.69, 150.76, 149.30, 148.57, 140.59, 138.12, 137.71, 137.65, 134.99, 134.28, 131.30, 131.20, 130.45, 130.23, 127.87, 127.74, 127.72, 127.62, 127.22, 127.01, 126.63, 126.56, 124.83. HRMS (ESI) Calcd for $C_{34}H_{24}N_2$ [M+H$^+$]: 461.2018; Found: 461.2013. GC-MS: 460.10. Crystal was obtained by slow evaporation of the CH_2Cl_2/hexane at room temperature.

Diethyl 6-methylpyridine-2,5-dicarboxylate (7a) [11]



Oil, 17 mg, 48% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.90 (s, 3H), 1.39–1.33 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.11, 164.81, 160.12, 149.69, 139.44, 128.65, 122.24, 62.37, 61.83, 25.08, 14.40, 14.35. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1729 cm^{-1}, ν_{C-O-C} 1267, 1264 cm^{-1}. HRMS (ESI) Calcd for $C_{12}H_{15}NO_4$ [M+H$^+$]: 238.1079; Found: 238.1073. GC-MS: 237.05.

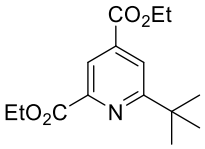
Diethyl 6-methylpyridine-2,4-dicarboxylate (8a) [12]



Oil, 18 mg, 51% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 0.7 Hz, 1H), 7.88 (d, *J* = 1.2 Hz, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.72 (s, 3H), 1.46 –

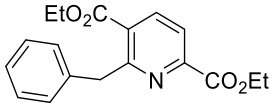
1.40 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.67, 164.50, 160.10, 148.69, 138.99, 125.76, 121.41, 62.03, 61.92, 24.49, 14.17, 14.0. MS (EI): m/z calcd. for $C_{12}H_{15}NO_4$: 237.10 GC-MS: m/z 237.10.

Diethyl 2-(tert-butyl)pyridine-3,5-dicarboxylate (8b)



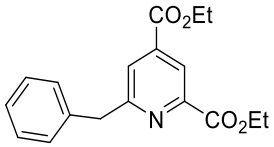
Oil, 29 mg, 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 1.2 Hz, 1H), 8.06 (d, *J* = 1.2 Hz, 1H), 4.45 (dq, *J* = 11.3, 7.1 Hz, 4H), 1.48 – 1.38 (m, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.16, 165.28, 165.23, 148.44, 139.11, 121.87, 121.35, 62.11, 61.93, 38.20, 30.20, 14.43, 14.39. MS (EI): m/z calcd. for $C_{15}H_{21}NO_4$: 279.15 GC-MS: m/z 279.10.

Diethyl 6-benzylpyridine-2,5-dicarboxylate (7c)



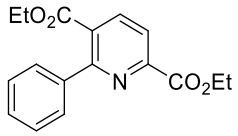
Colorless oil, 13 mg, 30% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.20 (m, 4H), 7.17 – 7.12 (m, 1H), 4.67 (s, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.96 (s), 164.67 (s), 161.32 (s), 149.67 (s), 139.52 (s), 139.20 (s), 129.12 (s), 128.98 (s), 128.21 (s), 126.17 (s), 122.55 (s), 62.18 (s), 61.77 (s), 42.53 (s), 14.28 (s), 14.07 (s). MS (EI): m/z calcd. for $C_{18}H_{19}NO_4$: 313.13 GC-MS: m/z 313.10.

Diethyl 6-benzylpyridine-2,4-dicarboxylate (8c)



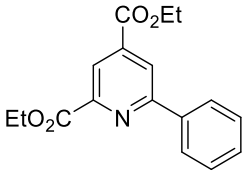
Colorless oil, 16 mg, 34% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 1.3 Hz, 1H), 7.79 (d, *J* = 1.4 Hz, 1H), 7.35 – 7.26 (m, 4H), 7.26 – 7.21 (m, 1H), 4.51 (q, *J* = 7.1 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.35 (s, 2H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.94 (s), 164.69 (s), 163.02 (s), 149.00 (s), 139.62 (s), 138.56 (s), 129.35 (s), 128.92 (s), 126.91 (s), 125.79 (s), 122.16 (s), 62.33 (s), 62.21 (s), 44.69 (s), 14.48 (s), 14.32 (s). MS (EI): m/z calcd. for $C_{18}H_{19}NO_4$: 313.13 GC-MS: m/z 313.05.

Diethyl 6-phenylpyridine-2,5-dicarboxylate (7d) [13]



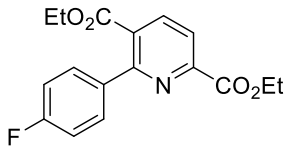
White solid, 19 mg, 42% yield. M.p.: 101-103 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.52 (m, 2H), 7.49 – 7.35 (m, 3H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.74 (s), 164.65, 158.74, 149.35, 139.35, 138.68, 130.22, 129.01, 128.83, 128.22, 122.63, 62.20, 61.85, 14.28, 13.61. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1721 cm^{-1}, ν_{C-O-C} 1267, 1263 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{17}NO_4$ [M+H$^+$]: 300.1236; Found: 300.1221. GC-MS: 299.05.

Diethyl 6-phenylpyridine-2,4-dicarboxylate (8d)



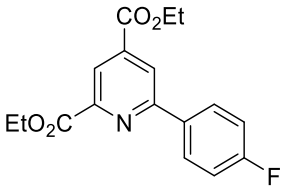
White solid, 23 mg, 52% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 1.3 Hz, 1H), 8.46 (d, *J* = 1.3 Hz, 1H), 8.24 – 8.05 (m, 2H), 7.61 – 7.41 (m, 3H), 4.50 (dq, *J* = 19.5, 7.1 Hz, 4H), 1.47 (dt, *J* = 12.2, 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.03, 164.79, 158.85, 149.51, 139.97, 137.87, 130.07, 129.07, 127.45, 122.82, 122.51, 62.33, 62.27, 14.46, 14.40. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1729 cm^{-1}, ν_{C-O-C} 1267, 1263 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{17}NO_4$ [M+H$^+$]: 300.1236; Found: 300.1236. GC-MS: 299.10.

Diethyl 6-(4-fluorophenyl)pyridine-2,5-dicarboxylate (7e)



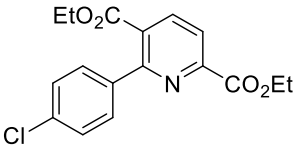
White solid, 9 mg, 19% yield. M.p.: 116-118 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.70 – 7.47 (m, 2H), 7.22 – 7.07 (m, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.63, 164.65, 163.61 (d, J_{CF} = 249.5 Hz), 157.77, 149.53, 139.01, 135.58 (d, J_{CF} = 3.3 Hz), 130.94 (d, J_{CF} = 8.5 Hz), 130.11, 122.86, 115.48, 115.31, 62.40, 62.08, 14.41, 13.86. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.35. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1728 cm^{-1}, ν_{C-O-C} 1267, 1263 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{16}FNO_4$ [M+H$^+$]: 318.1142; Found: 318.1129. GC-MS: 317.05.

Diethyl 6-(4-fluorophenyl)pyridine-2,4-dicarboxylate (8e)



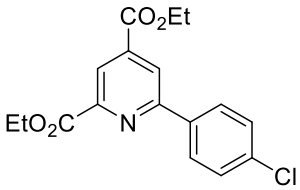
White solid, 24 mg, 50% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, J = 1.2 Hz, 1H), 8.41 (d, J = 1.2 Hz, 1H), 8.17 – 8.09 (m, 2H), 7.19 (t, J = 8.7 Hz, 2H), 4.50 (dq, J = 18.2, 7.1 Hz, 4H), 1.47 (dt, J = 11.2, 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.92, 164.69, 164.25 (d, J_{CF} = 249.5 Hz), 157.76, 149.50, 140.08, 134.05, 129.40 (d, J_{CF} = 8.6 Hz), 122.45 (d, J_{CF} = 3.5 Hz), 116.17, 115.99, 62.39, 62.31, 14.46, 14.40. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.52. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1722 cm^{-1}, ν_{C-O-C} 1267, 1264 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{16}FNO_4$ [M+H$^+$]: 318.1142; Found: 318.1134. GC-MS: 317.05.

Diethyl 6-(4-chlorophenyl)pyridine-2,5-dicarboxylate (7f)



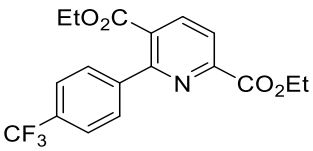
White solid, 10 mg, 21% yield. M.p.: 86-88 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.47 – 7.38 (m, 2H), 4.49 (q, J = 7.1 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1Hz, 5.2 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.45, 164.60, 157.71, 149.60, 139.09, 137.92, 135.44, 130.39, 130.07, 128.57, 123.05, 62.43, 62.14, 14.41, 13.86. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1722 cm^{-1}, ν_{C-O-C} 1267, 1263 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{16}ClNO_4$ [M+H$^+$]: 334.0846; Found: 334.0833. GC-MS: 333.05.

Diethyl 6-(4-chlorophenyl)pyridine-2,4-dicarboxylate (8f)



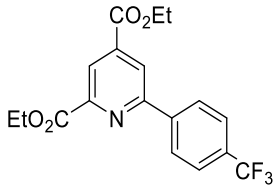
White solid, 21 mg, 42% yield. M.p.: 100-102 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, J = 1.2 Hz, 1H), 8.42 (d, J = 1.2 Hz, 1H), 8.09 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 4.50 (dq, J = 18.0, 7.1 Hz, 4H), 1.47 (dt, J = 11.0, 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.85, 164.62, 157.56, 149.57, 140.14, 136.36, 136.25, 129.29, 128.71, 122.74, 122.54, 62.43, 62.34, 14.45, 14.39. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1730 cm^{-1}, ν_{C-O-C} 1267, 1263 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{16}ClNO_4$ [M+H$^+$]: 334.0846; Found: 334.0832. GC-MS: 333.05.

Diethyl 6-(4-(trifluoromethyl)phenyl)pyridine-2,5-dicarboxylate (7g)



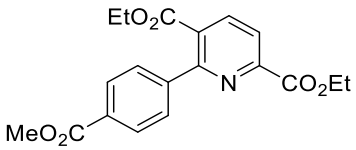
White solid, 15 mg, 27% yield. M.p.: 56-58 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.72 – 7.65 (m, 4H), 4.49 (q, J = 7.1 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H), 1.07 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 166.11 (s), 163.78 (s), 156.39 (s), 149.01 (s), 143.03 (s), 139.66 (s), 129.66 (s), 129.42 (s), 129.17 (q, J_{CF} = 31.5 Hz), 125.06 (q, J_{CF} = 3.7 Hz), 124.19 (q, J_{CF} = 272.2 Hz), 123.73 (s), 61.71 (s), 61.68 (s), 14.06 (s), 13.34 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.13. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1723 cm^{-1}, ν_{C-O-C} 1267, 1264 cm^{-1}. HRMS (ESI) Calcd for $C_{18}H_{16}F_3NO_4$ [M+H$^+$]: 368.1110; Found: 368.1103. GC-MS: 367.10.

Diethyl 6-(4-(trifluoromethyl)phenyl)pyridine-2,4-dicarboxylate (8g)



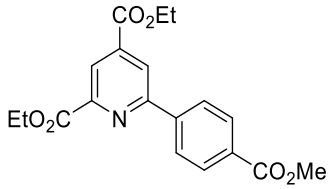
White solid, 26 mg, 47% yield. M.p.: 107-109 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, J = 1.1 Hz, 1H), 8.49 (d, J = 1.1 Hz, 1H), 8.25 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 4.51 (dq, J = 17.4, 7.1 Hz, 4H), 1.47 (dt, J = 10.4, 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.73, 164.49, 157.22, 149.78, 141.10, 140.32, 134.57, 131.85 (q, J_{CF} = 31.5 Hz), 128.42 (q, J_{CF} = 267.12 Hz), 127.79, 126.02 (q, J_{CF} = 3.7 Hz), 123.33, 123.06, 62.51, 62.41, 14.44, 14.38. ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.24. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1729 cm^{-1}, ν_{C-O-C} 1267, 1263 cm^{-1}. HRMS (ESI) Calcd for $C_{18}H_{16}F_3NO_4$ [M+H$^+$]: 368.1110; Found: 368.1112. GC-MS: 367.10.

Diethyl 6-(4-(methoxycarbonyl)phenyl)pyridine-2,5-dicarboxylate (7h)



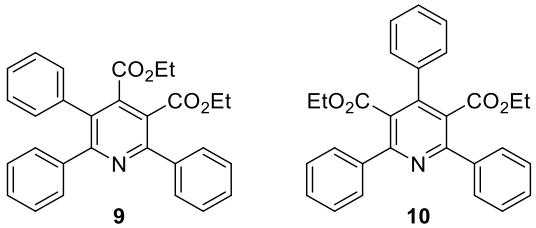
White solid, 16 mg, 30% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 – 8.03 (m, 4H), 7.66 (d, J = 8.0 Hz, 2H), 4.49 (q, J = 14.1, 7.0 Hz, 2H), 4.18 (q, J = 14.1, 7.1 Hz, 2H), 3.95 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H), 1.06 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.13, 166.80, 164.43, 157.85, 149.55, 143.74, 139.02, 130.42, 130.18, 129.48, 128.96, 123.25, 62.35, 62.04, 52.26, 14.27, 13.67. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1722 cm^{-1}, ν_{C-O-C} 1267, 1263 cm^{-1}. HRMS (ESI) Calcd for $C_{19}H_{19}NO_6$ [M+H$^+$]: 358.1291; Found: 358.1277. GC-MS: 357.05. Crystal was obtained by slow evaporation of the CH_2Cl_2/hexane at room temperature.

Diethyl 6-(4-(methoxycarbonyl)phenyl)pyridine-2,4-dicarboxylate (8h)



White solid, 24 mg, 46% yield. M.p.: 97-99 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.1 Hz, 1H), 8.49 (d, *J* = 1.1 Hz, 1H), 8.19 (m, 4H), 4.50 (dq, *J* = 18.8, 7.1 Hz, 4H), 3.95 (s, 3H), 1.47 (dt, *J* = 11.7, 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.88, 164.82, 164.57, 157.63, 149.75, 141.88, 140.25, 131.41, 130.35, 127.44, 123.23, 62.49, 62.42, 52.43, 14.46, 14.41. FT-IR (CH_2Cl_2): $\nu_{C=O}$ 1725 cm^{-1}, ν_{C-O-C} 1267, 1263 cm^{-1}. HRMS (ESI) Calcd for $C_{19}H_{19}NO_6$ [M+H$^+$]: 358.1291; Found: 358.1283. GC-MS: 357.30. Crystal was obtained by slow evaporation of the CH_2Cl_2/hexane at room temperature.

Diethyl 2,5,6-triphenylpyridine-3,4-dicarboxylate (9) and diethyl 2,4,6-triphenylpyridine-3,5-dicarboxylate (10)



White solid, 58 mg, 86% NMR yield. Attempts to separate the two isomers through column chromatography were unsuccessful. Layering a CH_2Cl_2 solution of the product mixture with hexane at –30ºC provided single crystals some of which were suitable for XRD analysis. Both isomers were crystallographically characterized by our diligent work. HRMS (ESI) Calcd for $C_{29}H_{25}NO_4$ [M+H$^+$]: 452.1862; Found: 452.1767. GC-MS: 451.09.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 7H), 7.72 – 7.66 (m, 2H), 7.46 – 7.37 (m, 22H), 7.36 – 7.33 (m, 2H), 7.30 – 7.26 (m, 3H), 7.25 – 7.15 (m, 5H). For **9**: 4.16 (q, *J* = 7.1 Hz, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H). For **10**[14]: 3.88 (q, *J* = 7.1 Hz, 7H), 0.83 (t, *J* = 7.1 Hz, 11H).

4. NMR Spectra

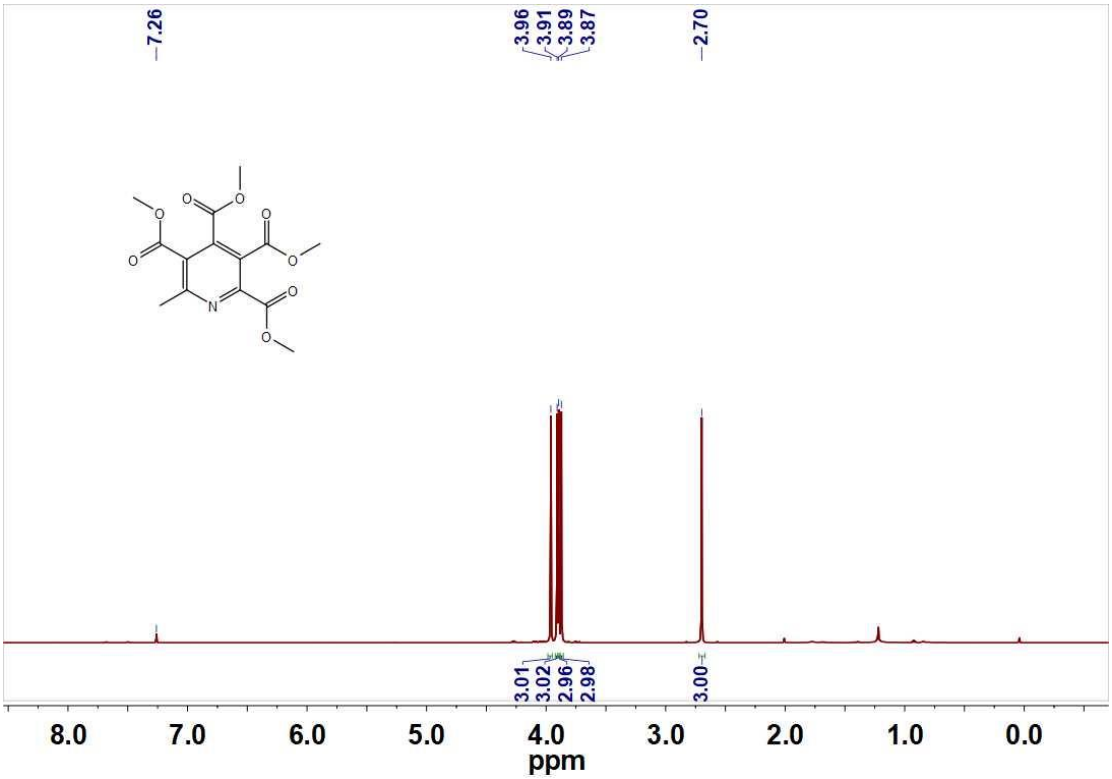


Figure S8. ^{1}H NMR spectrum of **5a** in $CDCl_3$

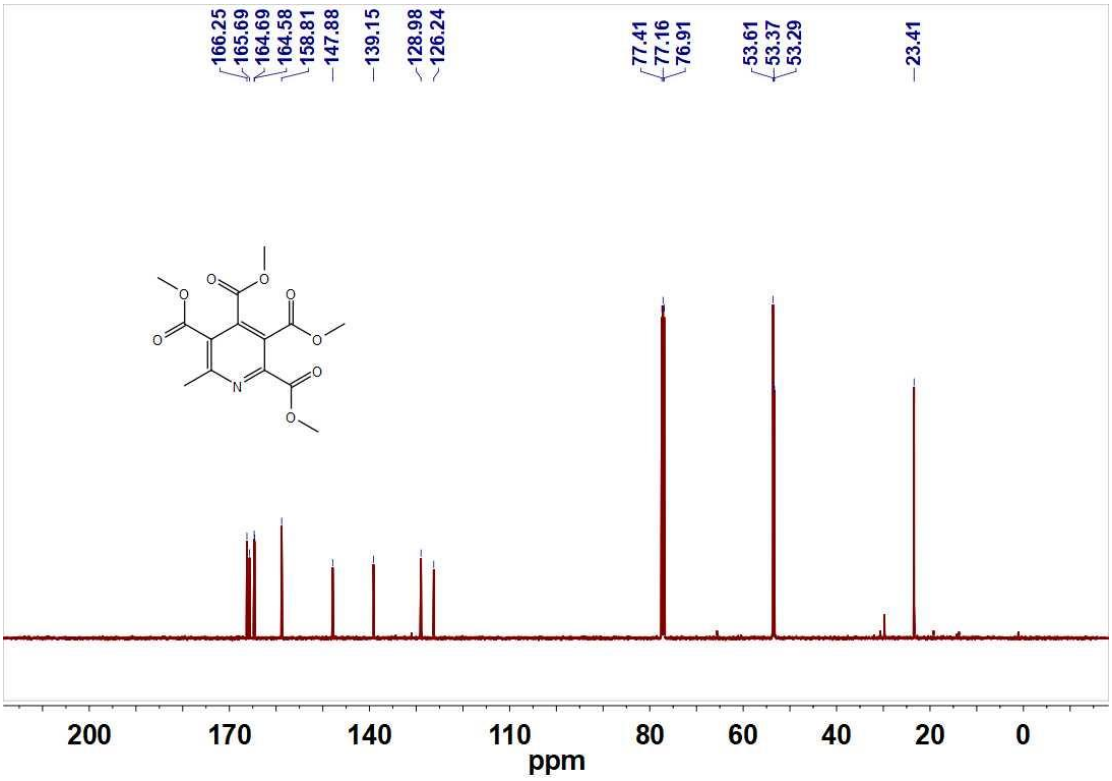


Figure S9. ^{13}C NMR spectrum of **5a** in $CDCl_3$

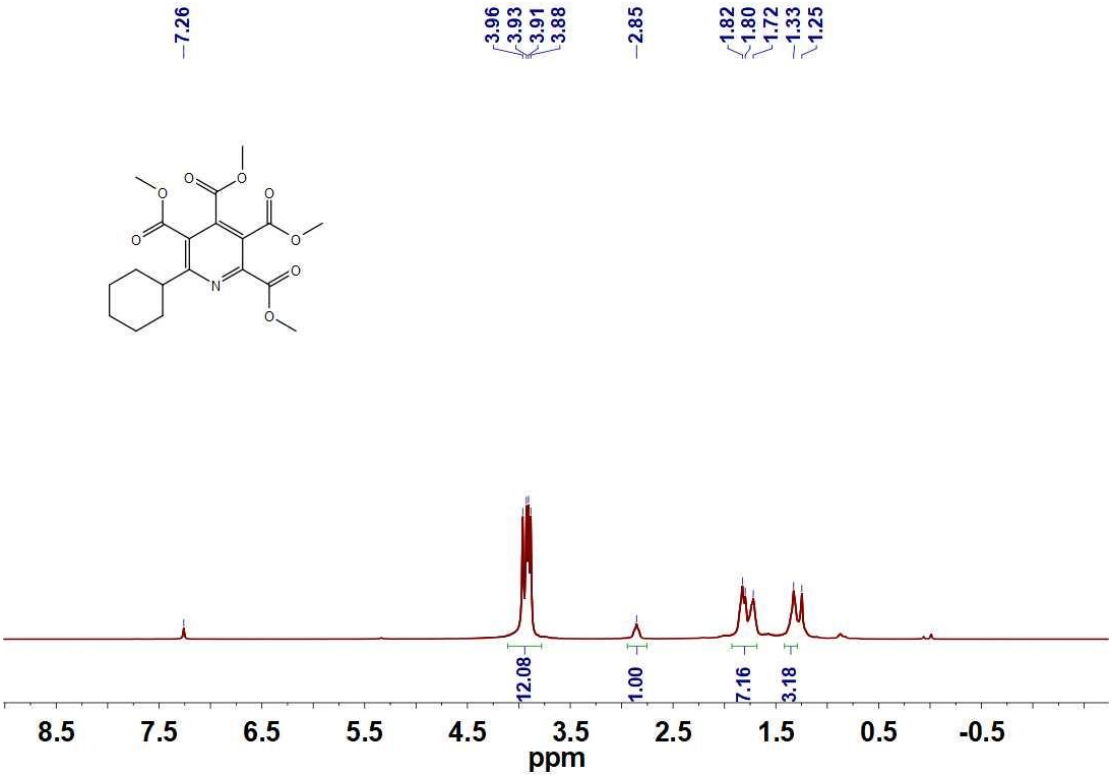


Figure S10. ^{1}H NMR spectrum of **5b** in $CDCl_3$

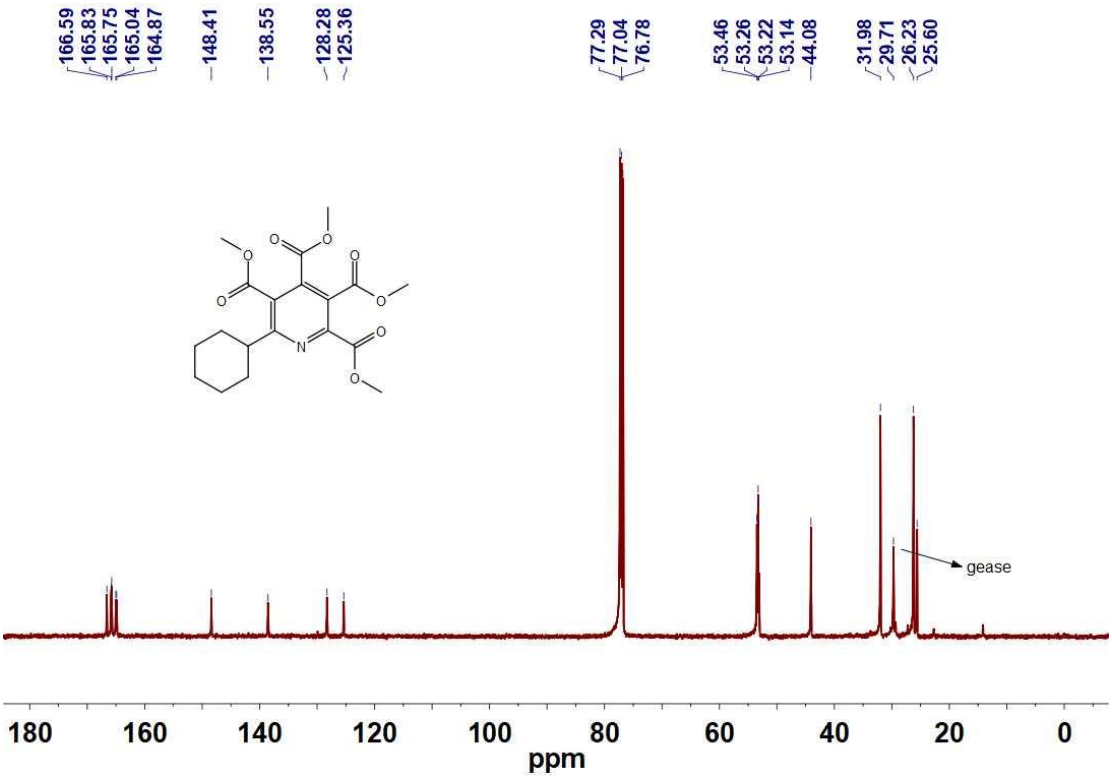


Figure S11. ^{13}C NMR spectrum of **5b** in $CDCl_3$

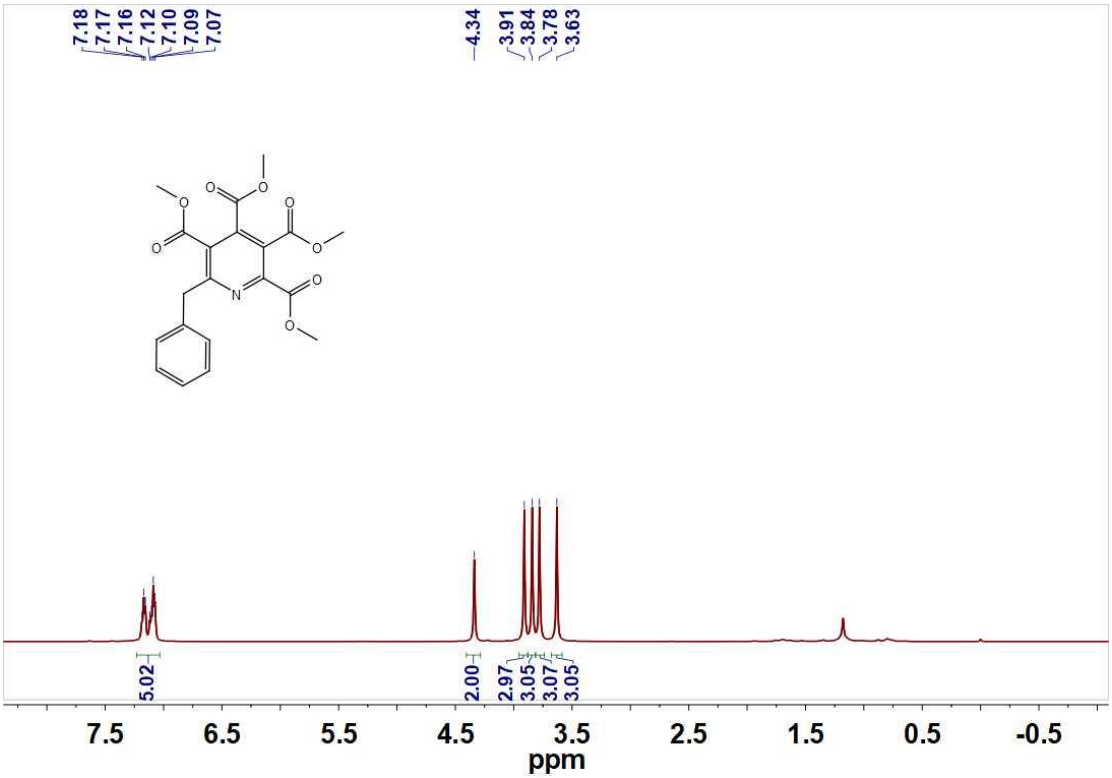


Figure S12. ^{1}H NMR spectrum of **5c** in $CDCl_3$

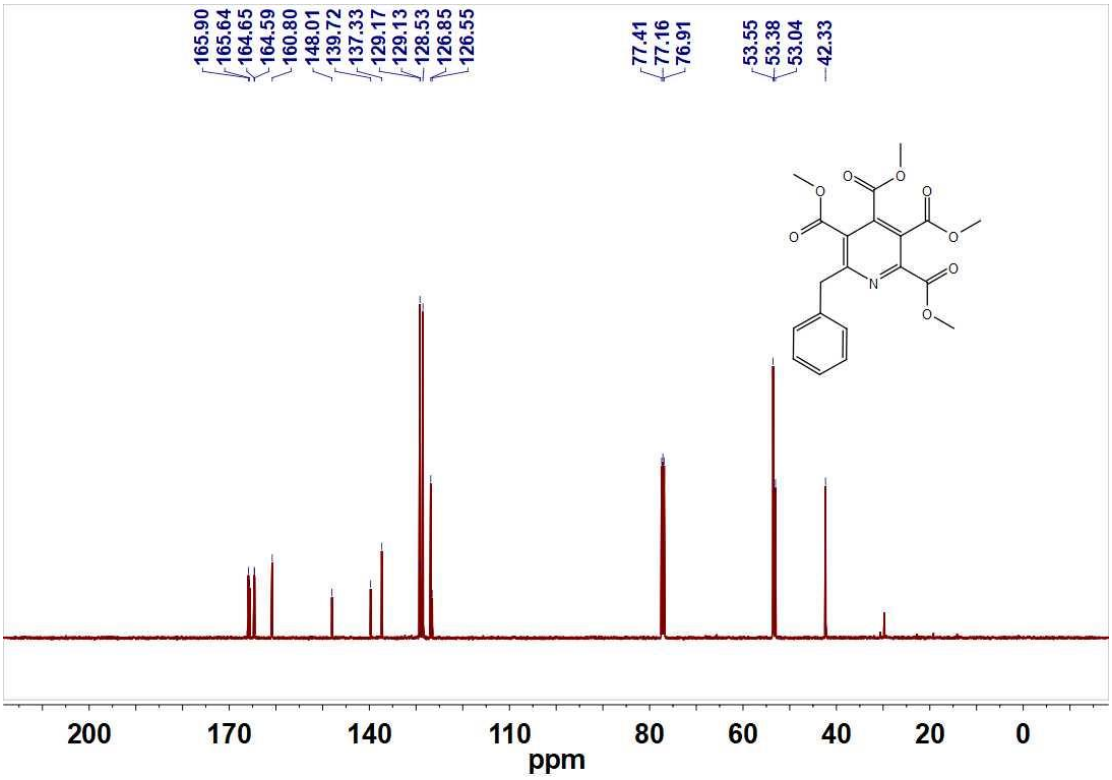


Figure S13. ^{13}C NMR spectrum of **5c** in $CDCl_3$

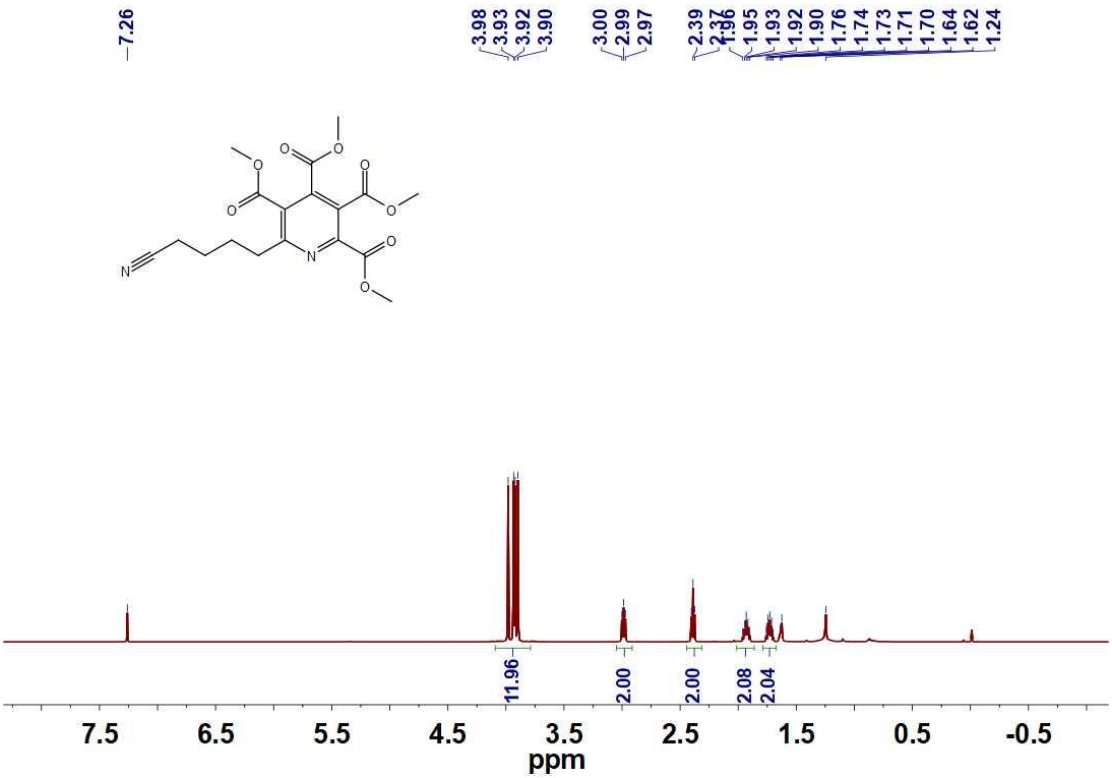


Figure S14. ^{1}H NMR spectrum of **5d** in $CDCl_3$

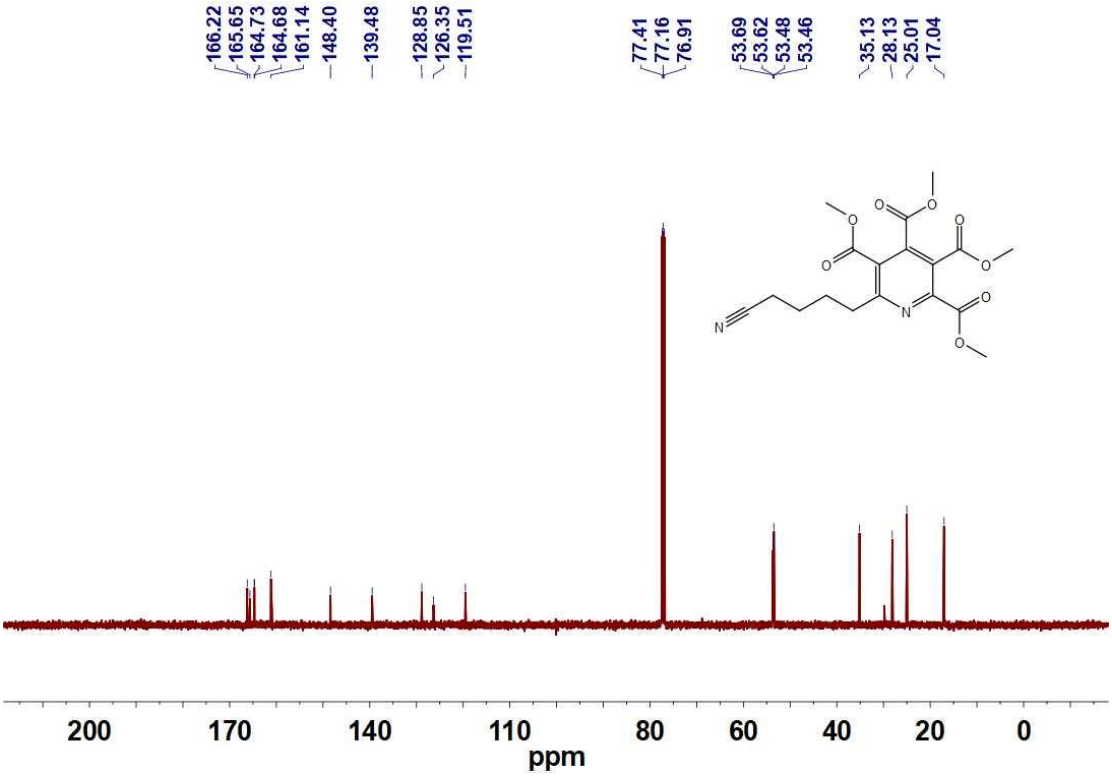


Figure S15. ^{13}C NMR spectrum of **5d** in $CDCl_3$

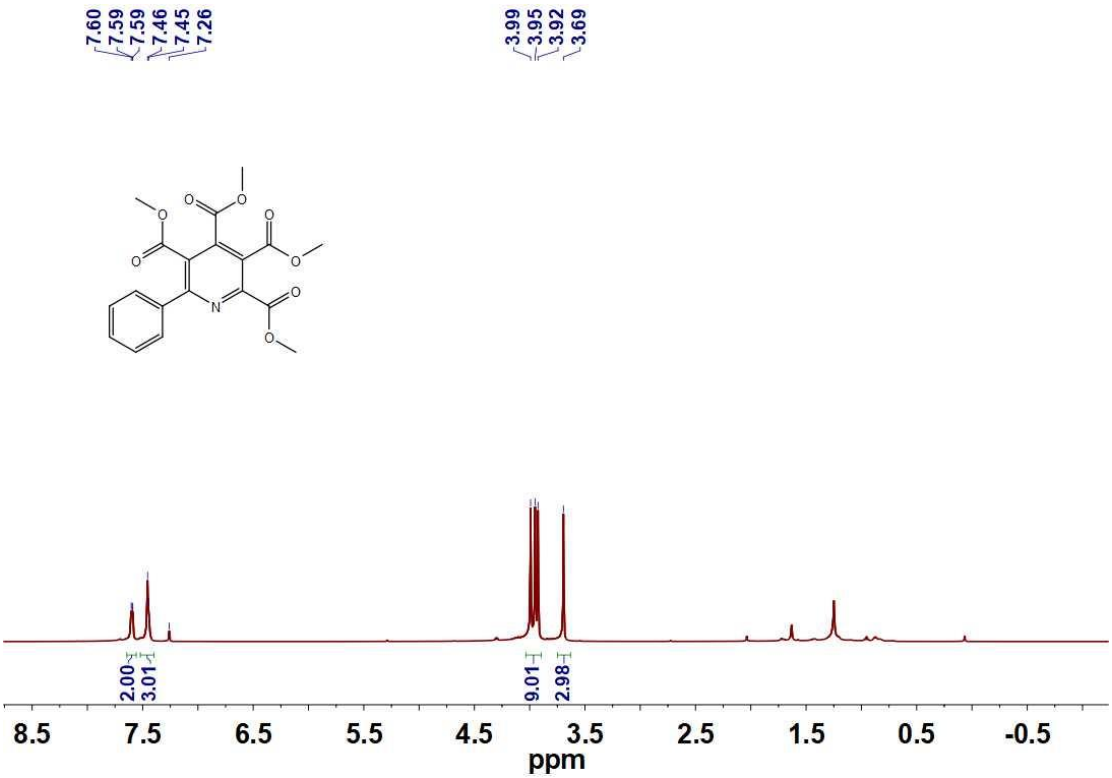


Figure S16. ^{1}H NMR spectrum of **5e** in $CDCl_3$

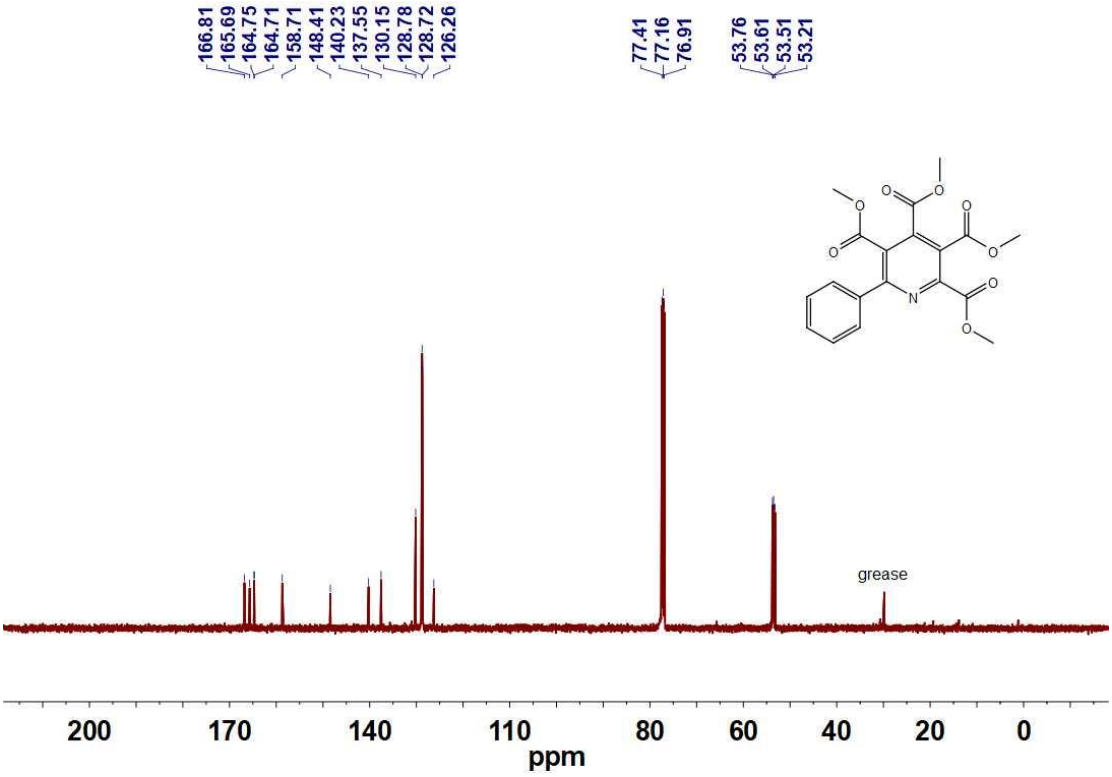


Figure S17. ^{13}C NMR spectrum of **5e** in $CDCl_3$

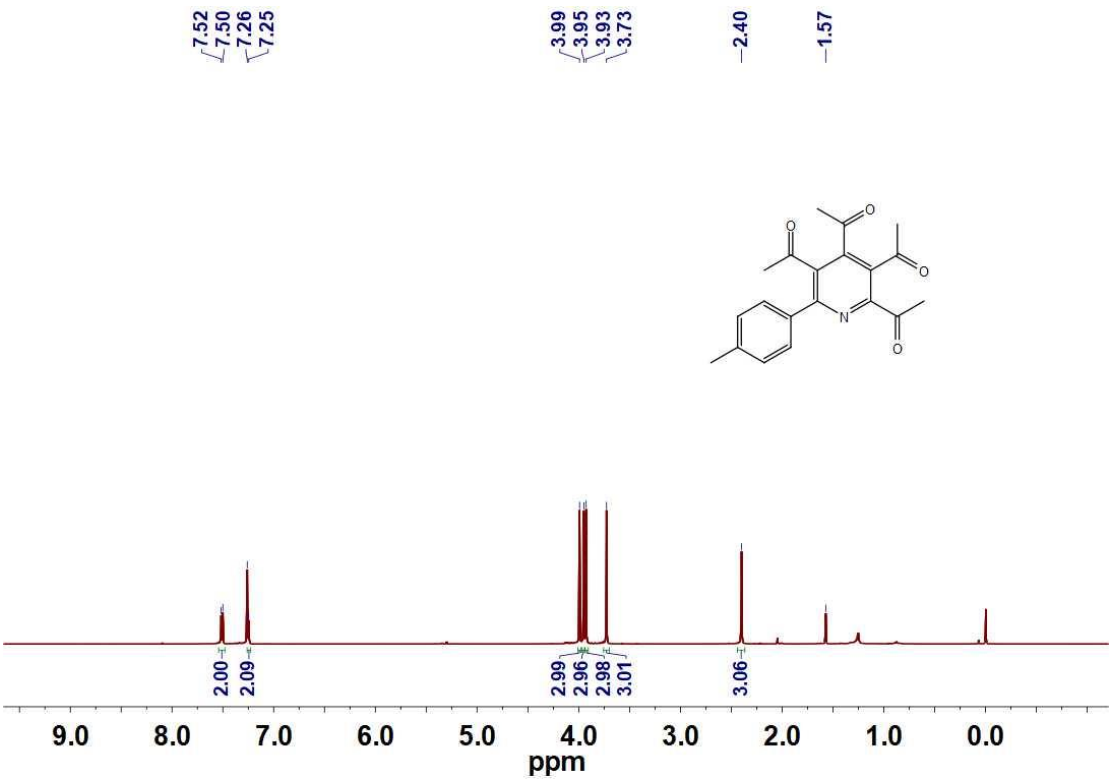


Figure S18. ^{1}H NMR spectrum of **5f** in $CDCl_3$

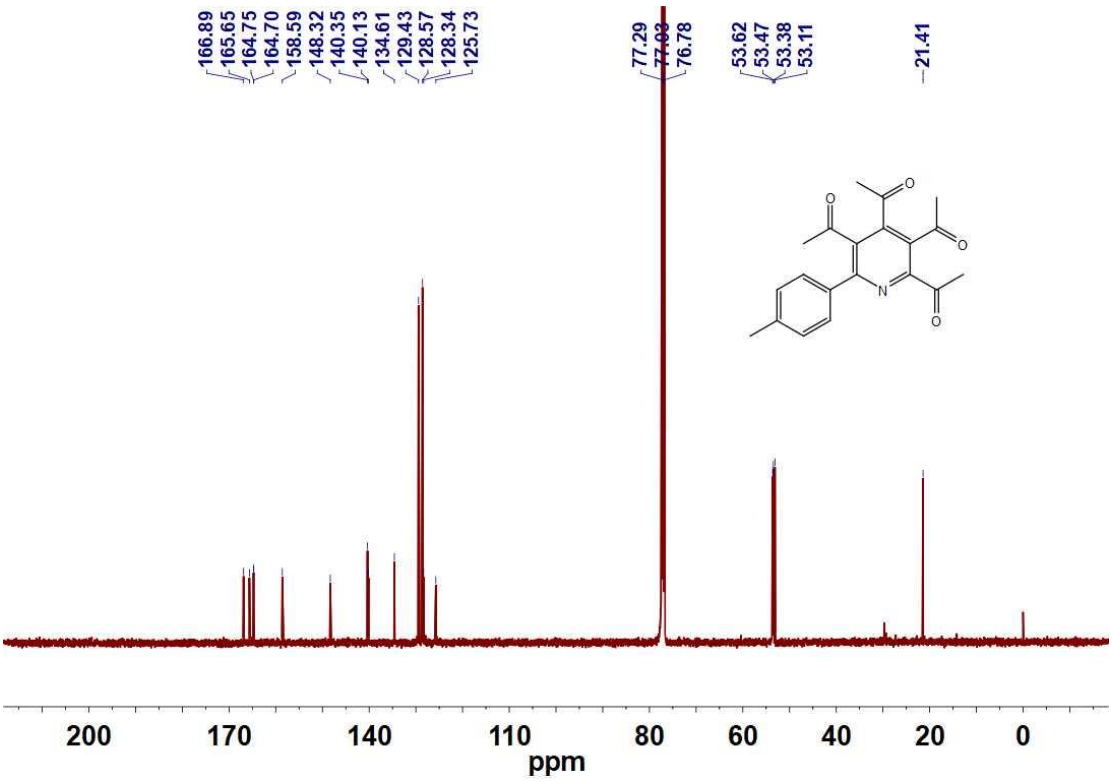


Figure S19. ^{13}C NMR spectrum of **5f** in $CDCl_3$

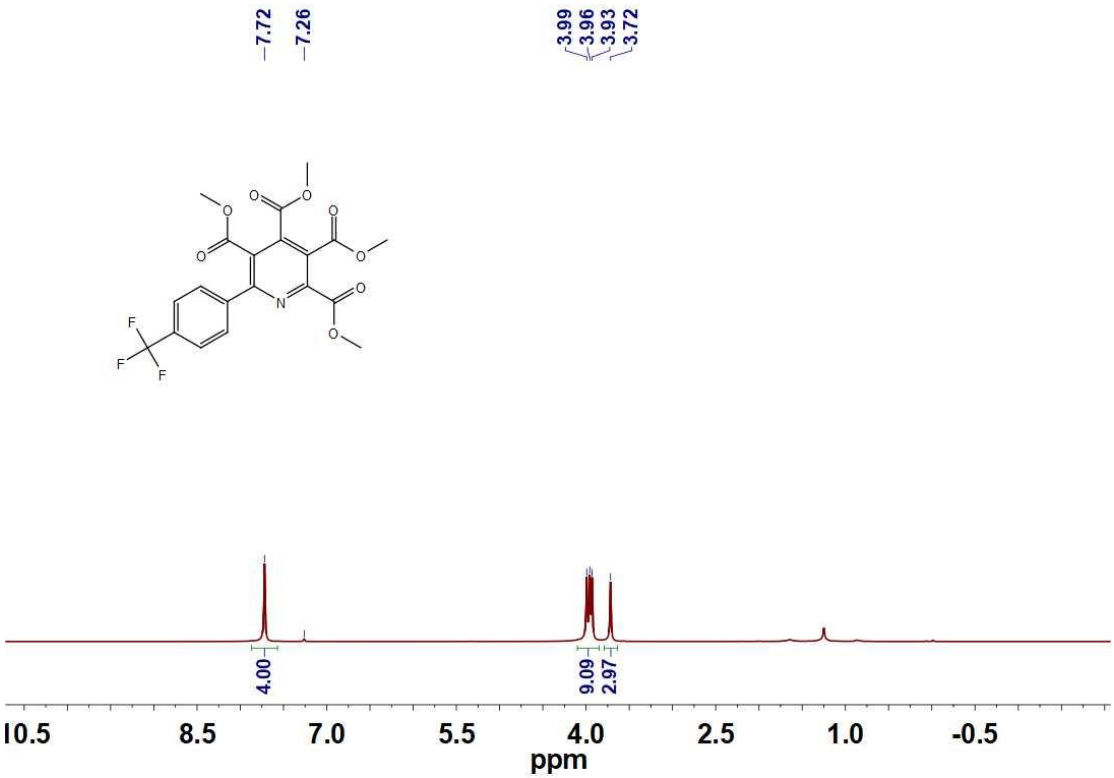


Figure S20. ^{1}H NMR spectrum of **5g** in $CDCl_3$

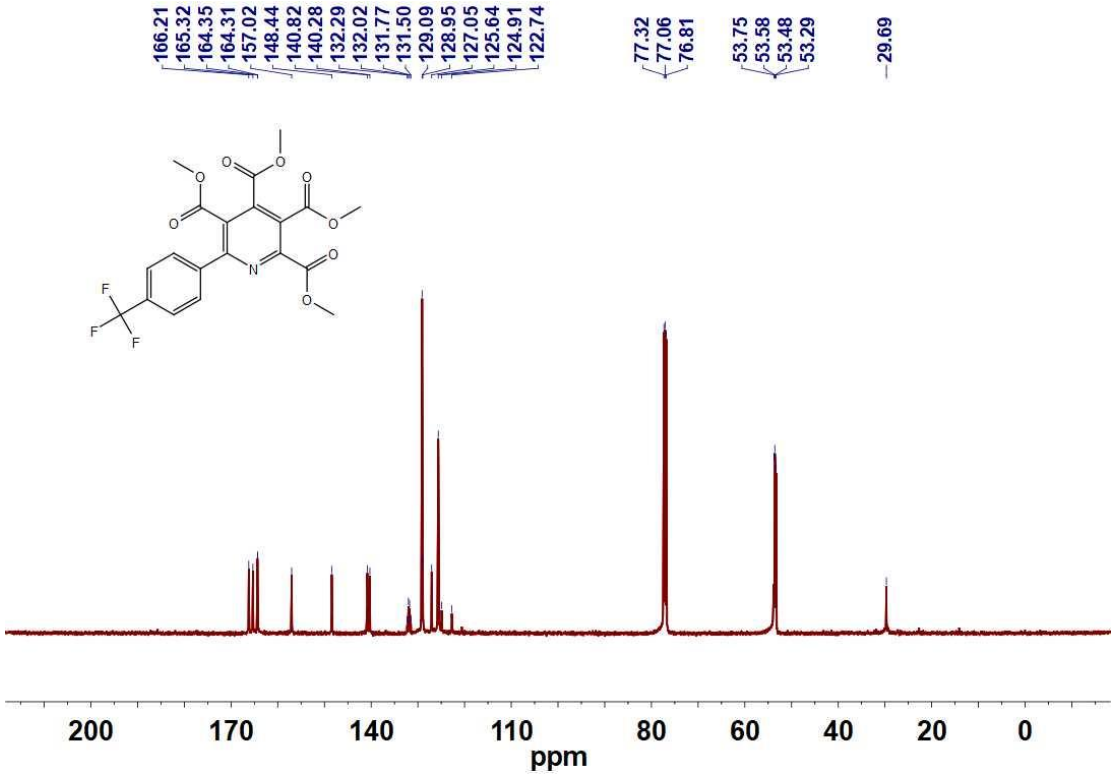


Figure S21. ^{13}C NMR spectrum of **5g** in $CDCl_3$

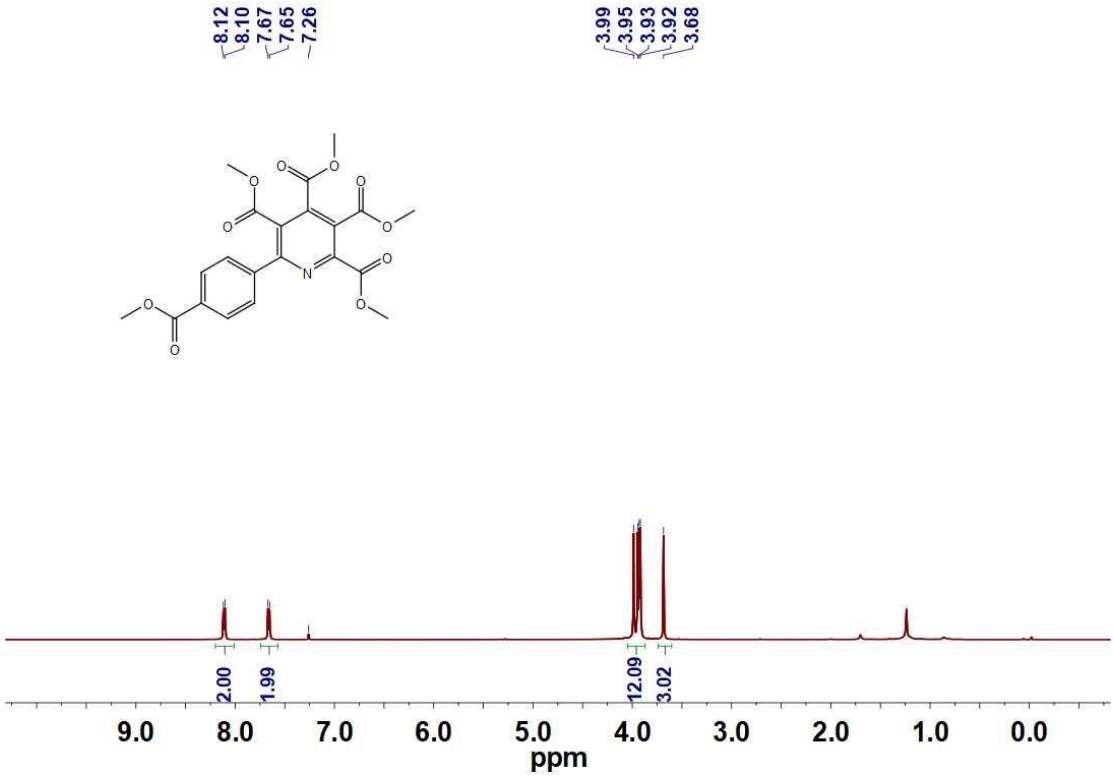


Figure S22. ^{1}H NMR spectrum of **5h** in $CDCl_3$

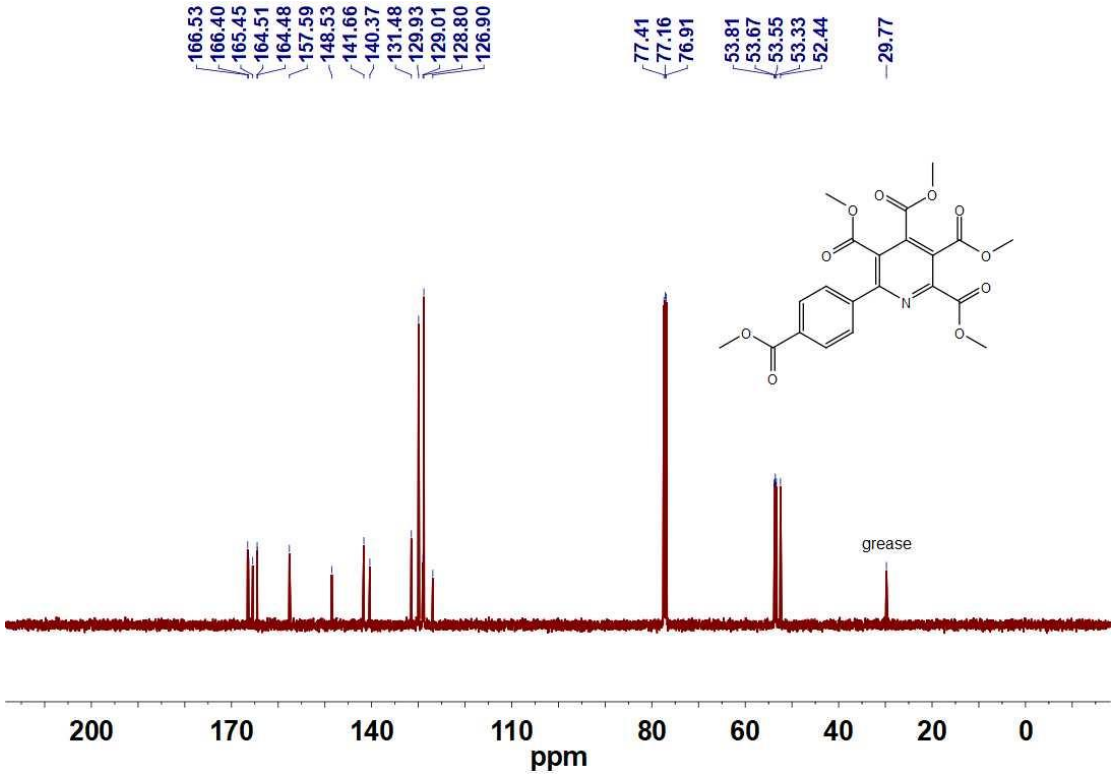


Figure S23. ^{13}C NMR spectrum of **5h** in $CDCl_3$

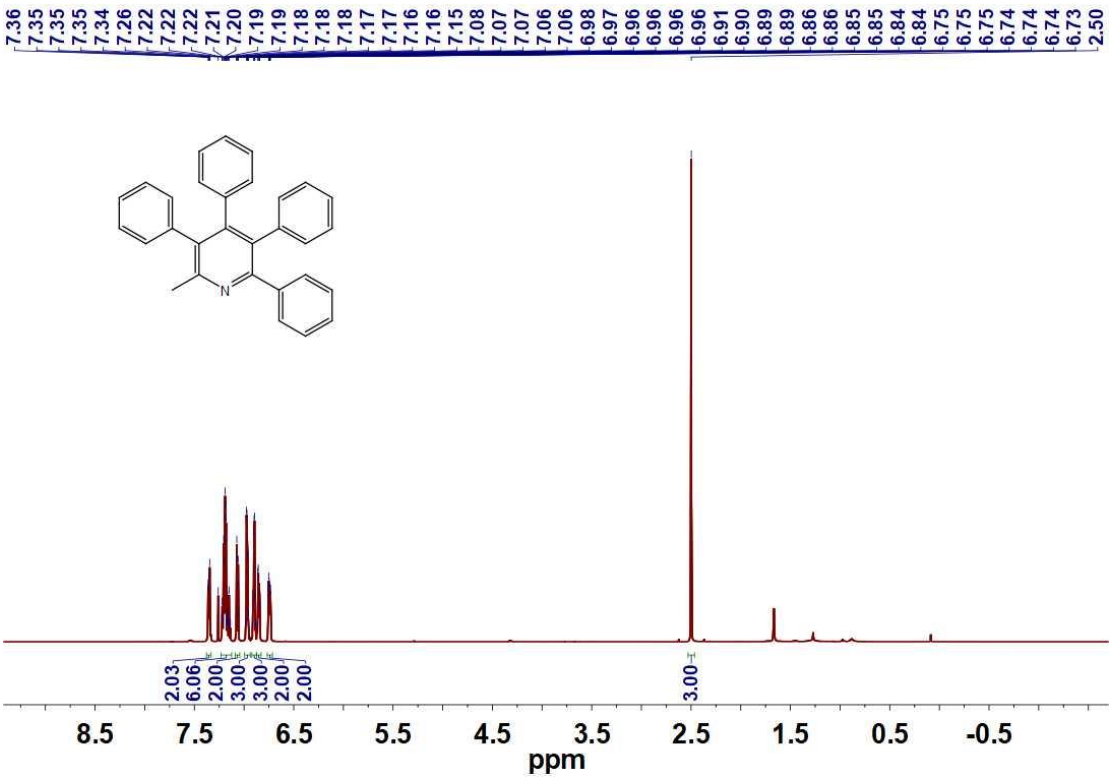


Figure S24. ^{1}H NMR spectrum of **6a** in $CDCl_3$

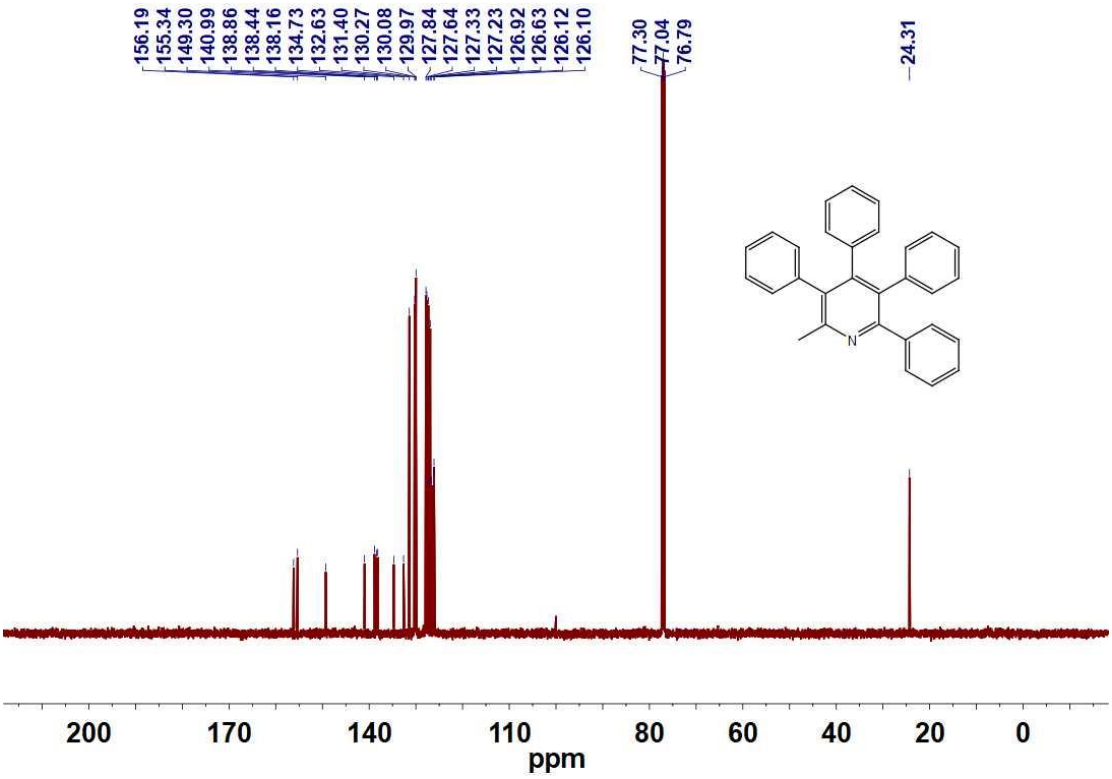


Figure S25. ^{13}C NMR spectrum of **6a** in $CDCl_3$

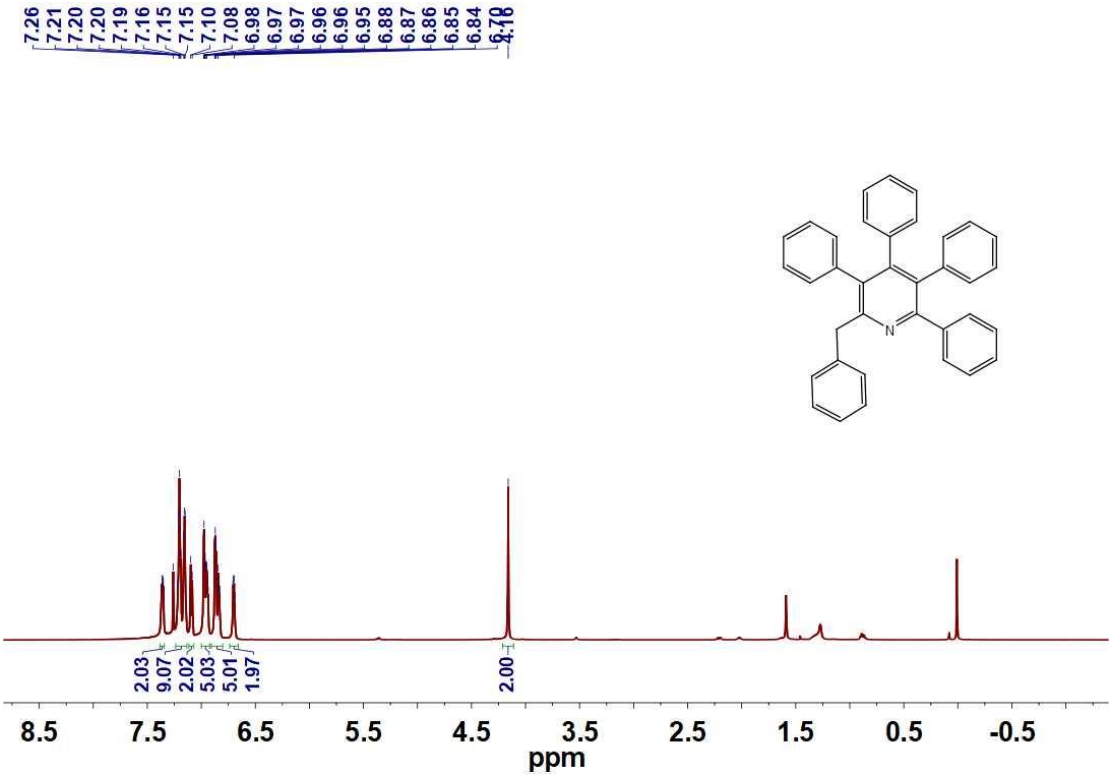


Figure S26. ^{1}H NMR spectrum of **6b** in $CDCl_3$

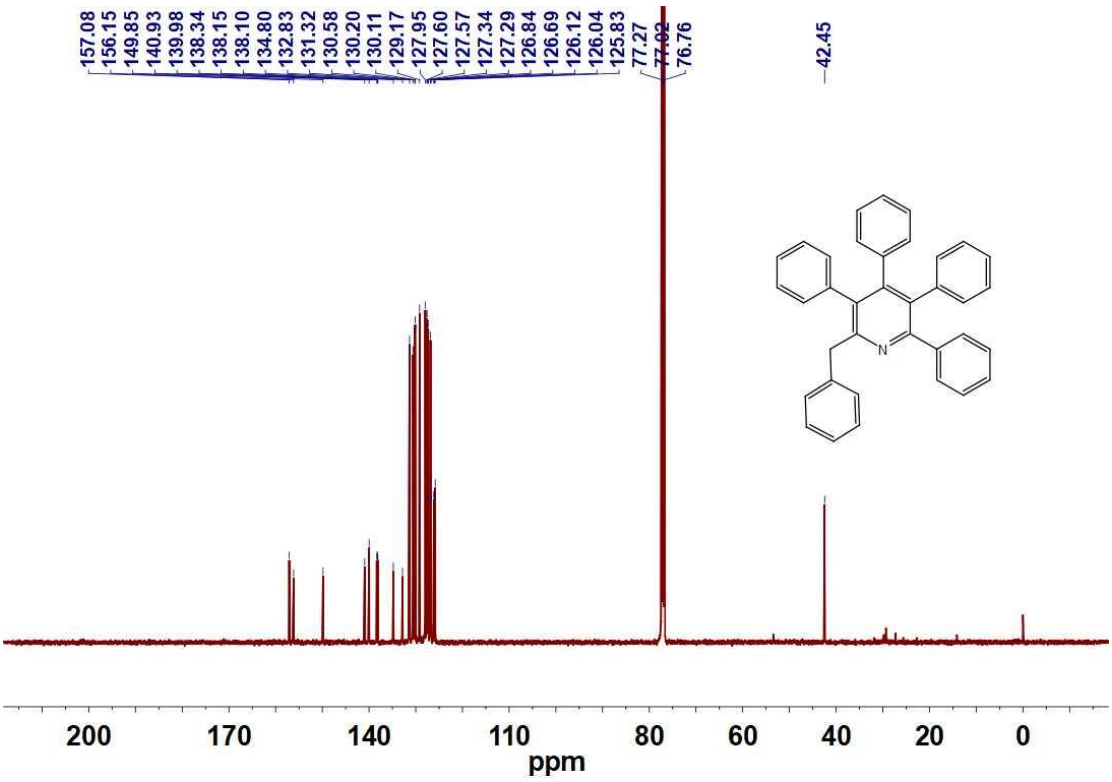


Figure S27. ^{13}C NMR spectrum of **6b** in $CDCl_3$

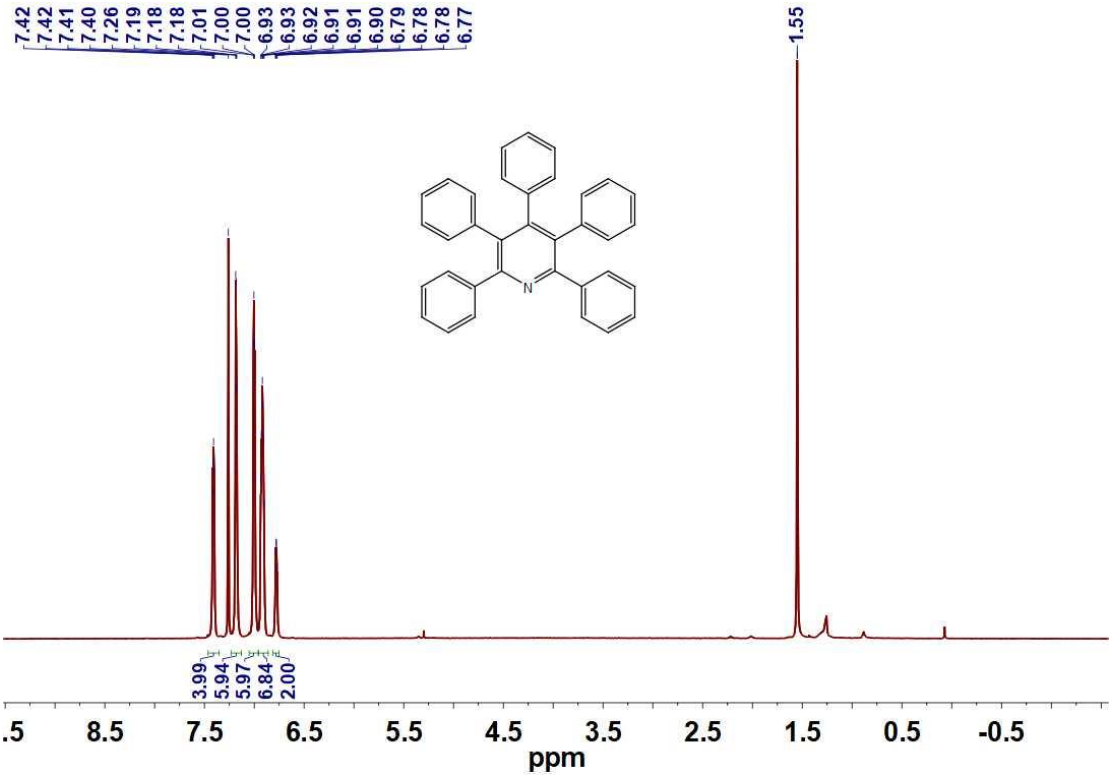


Figure S28. ^{1}H NMR spectrum of **6c** in $CDCl_3$

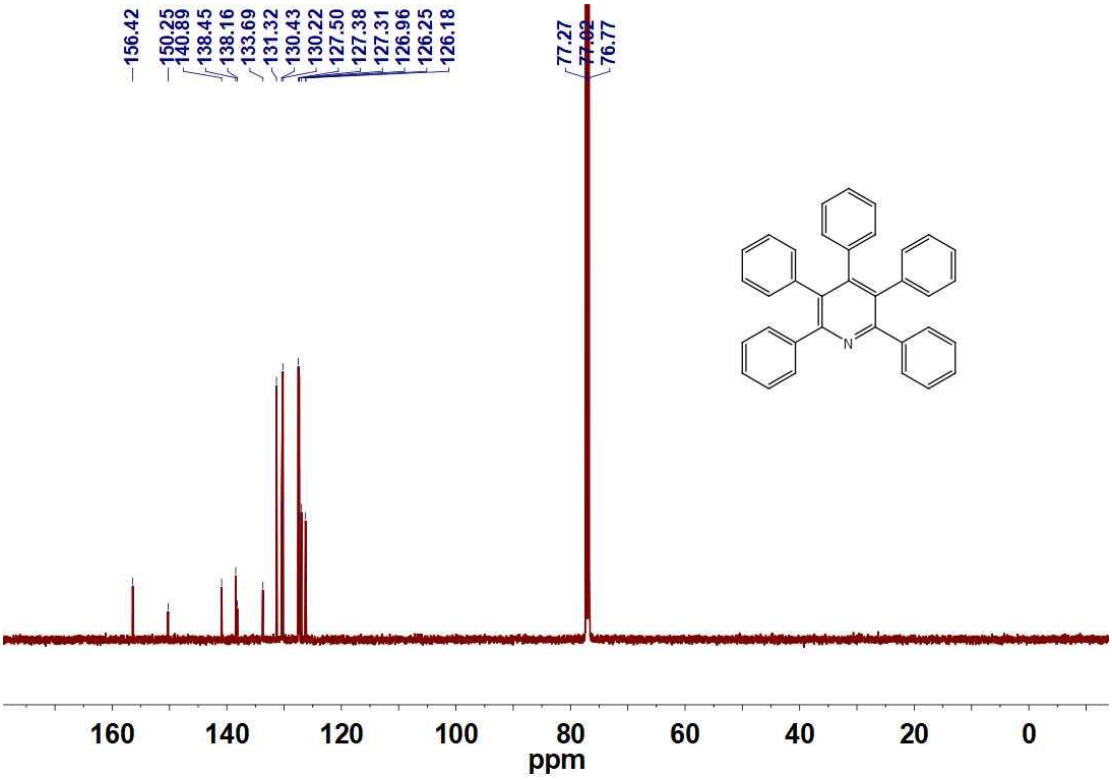


Figure S29. ^{13}C NMR spectrum of **6c** in $CDCl_3$

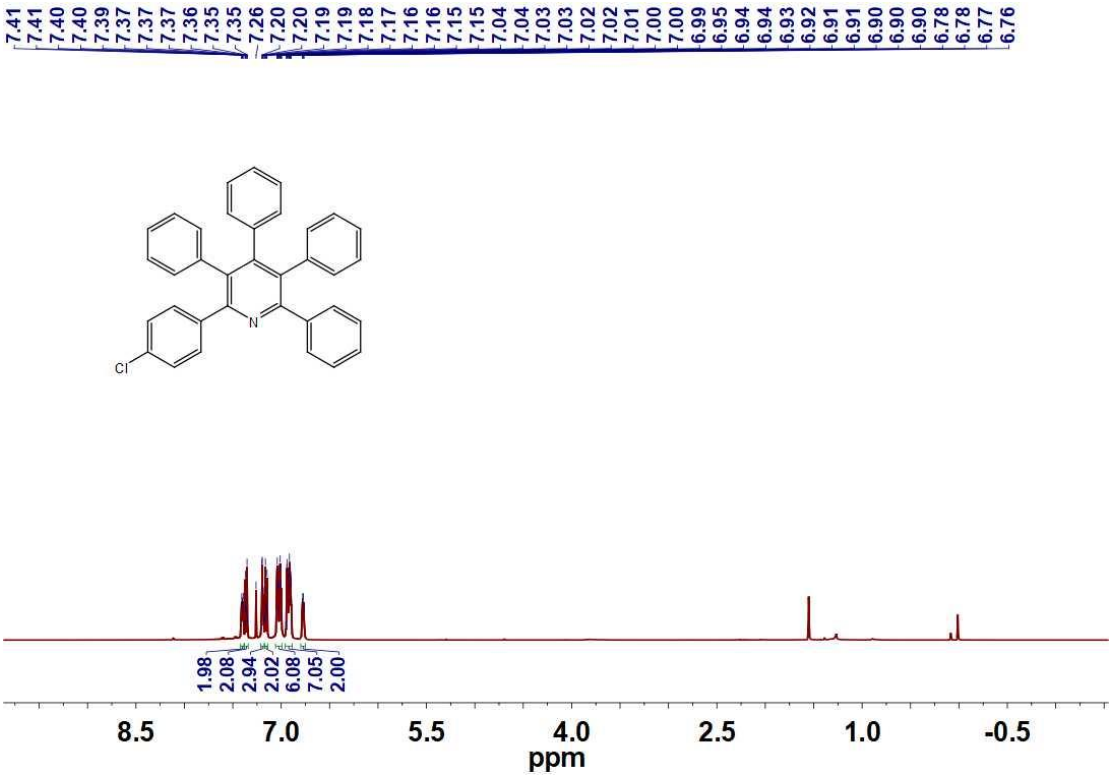


Figure S30. ^{1}H NMR spectrum of **6e** in $CDCl_3$

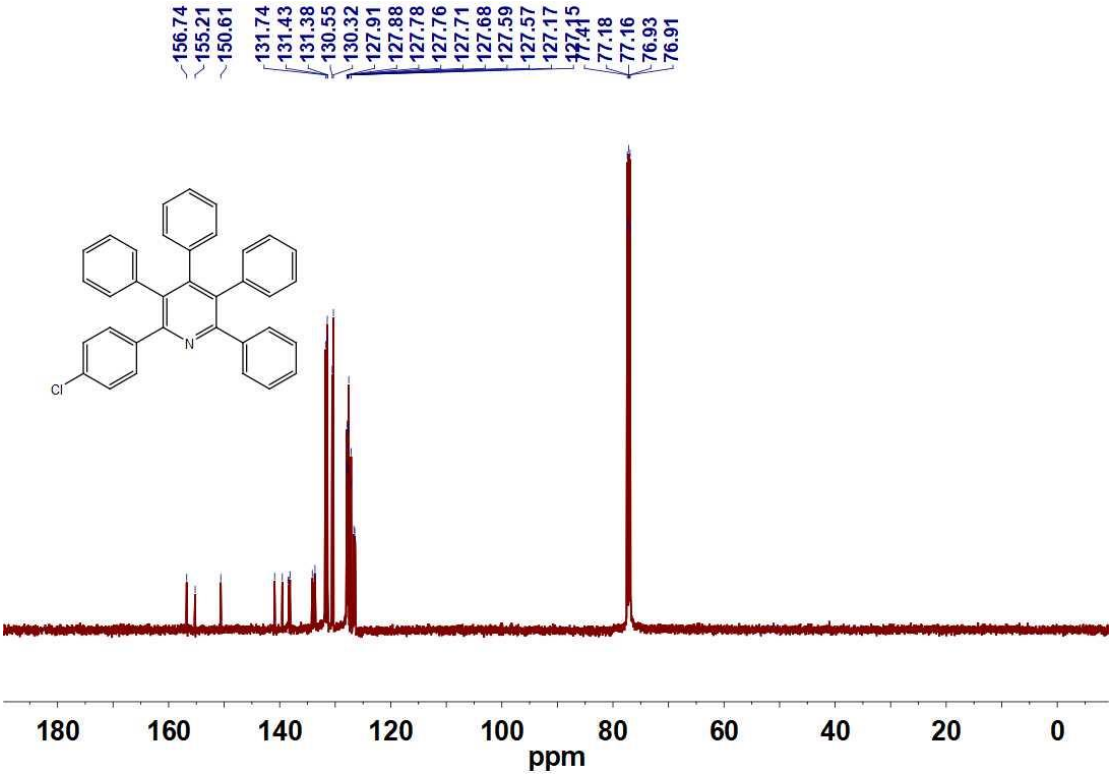


Figure S31. ^{13}C NMR spectrum of **6e** in $CDCl_3$

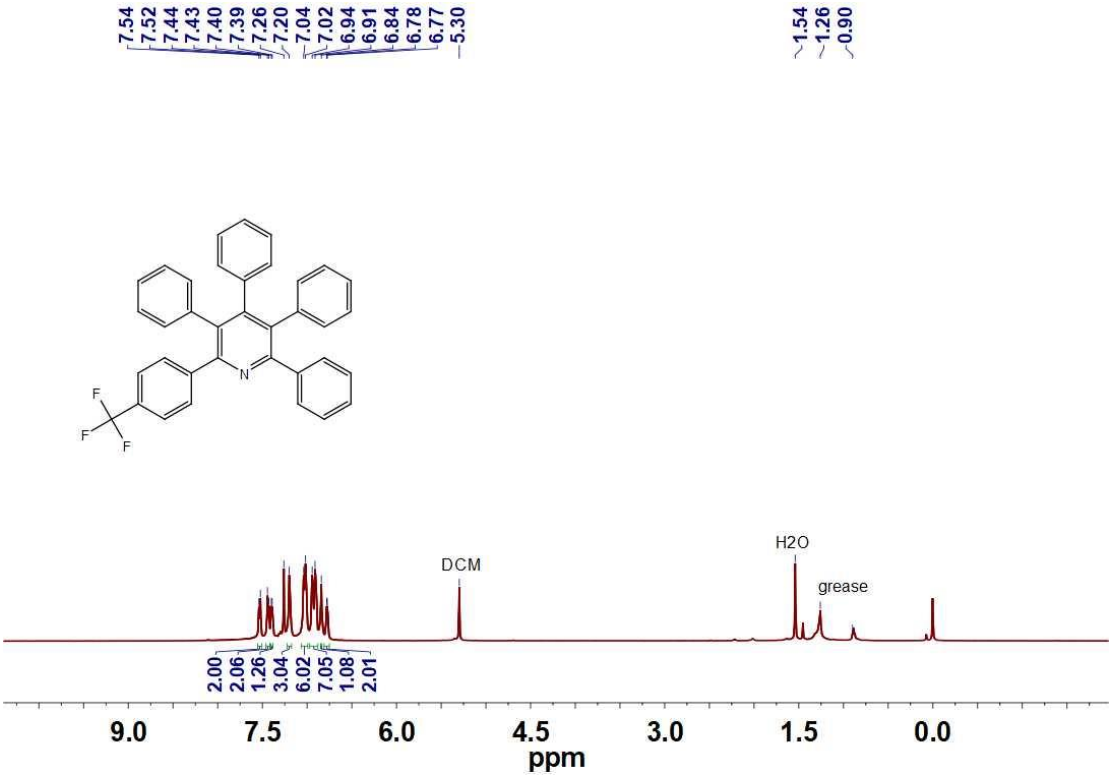


Figure S32. ^{1}H NMR spectrum of **6f** in $CDCl_3$

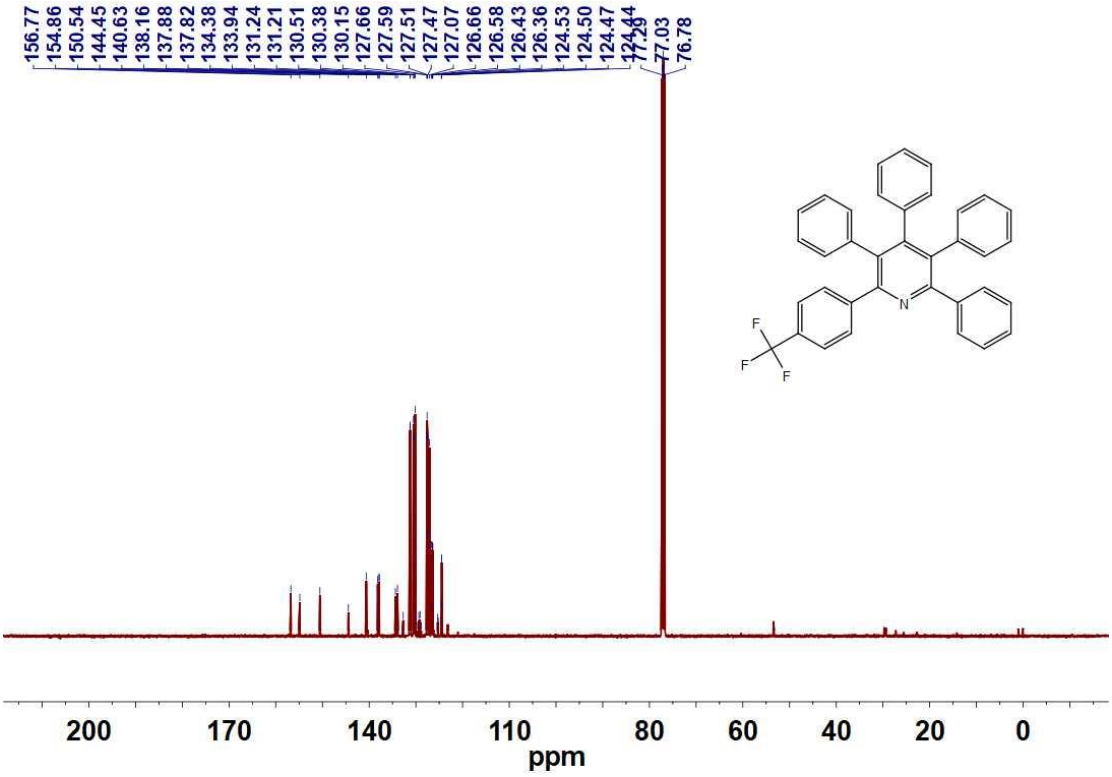


Figure S33. ^{13}C NMR spectrum of **6f** in $CDCl_3$

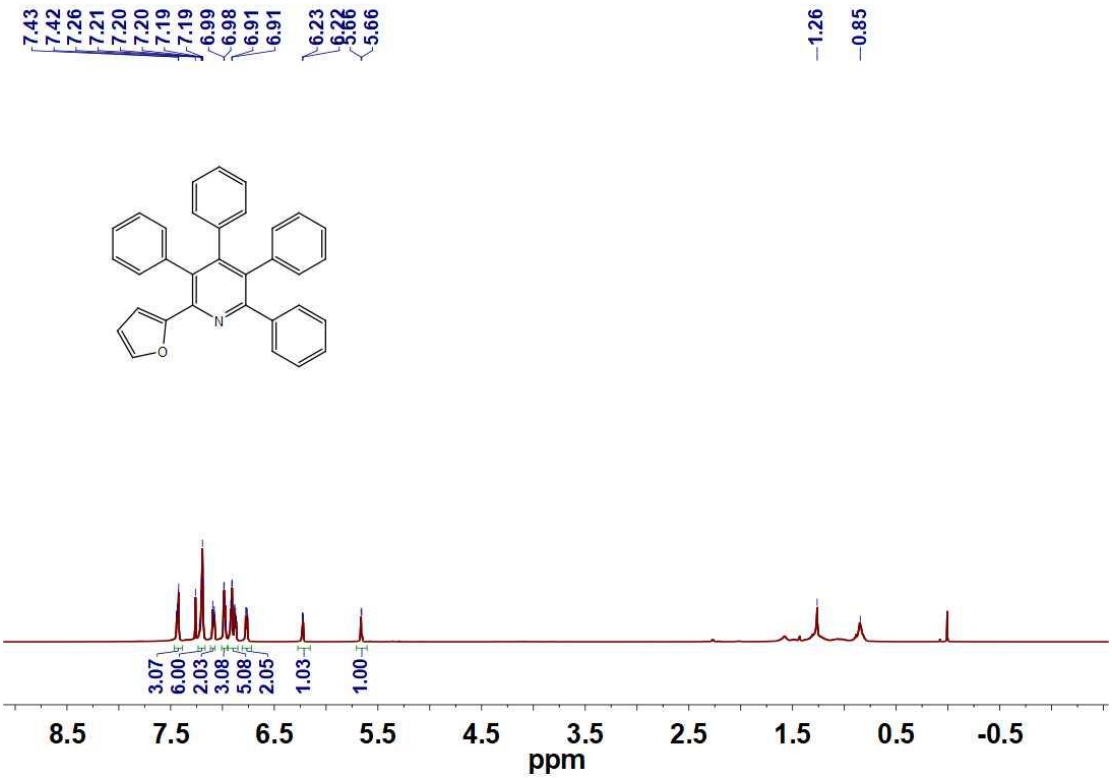


Figure S34. ^{1}H NMR spectrum of **6g** in $CDCl_3$

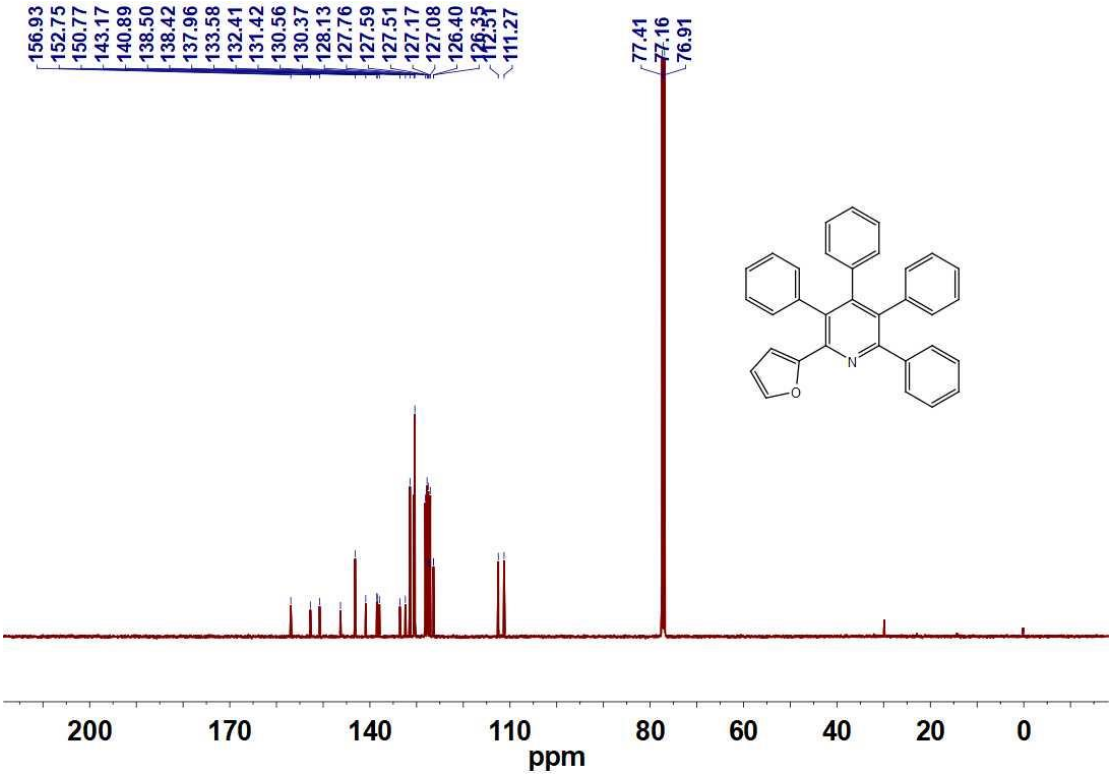


Figure S35. ^{13}C NMR spectrum of **6g** in $CDCl_3$

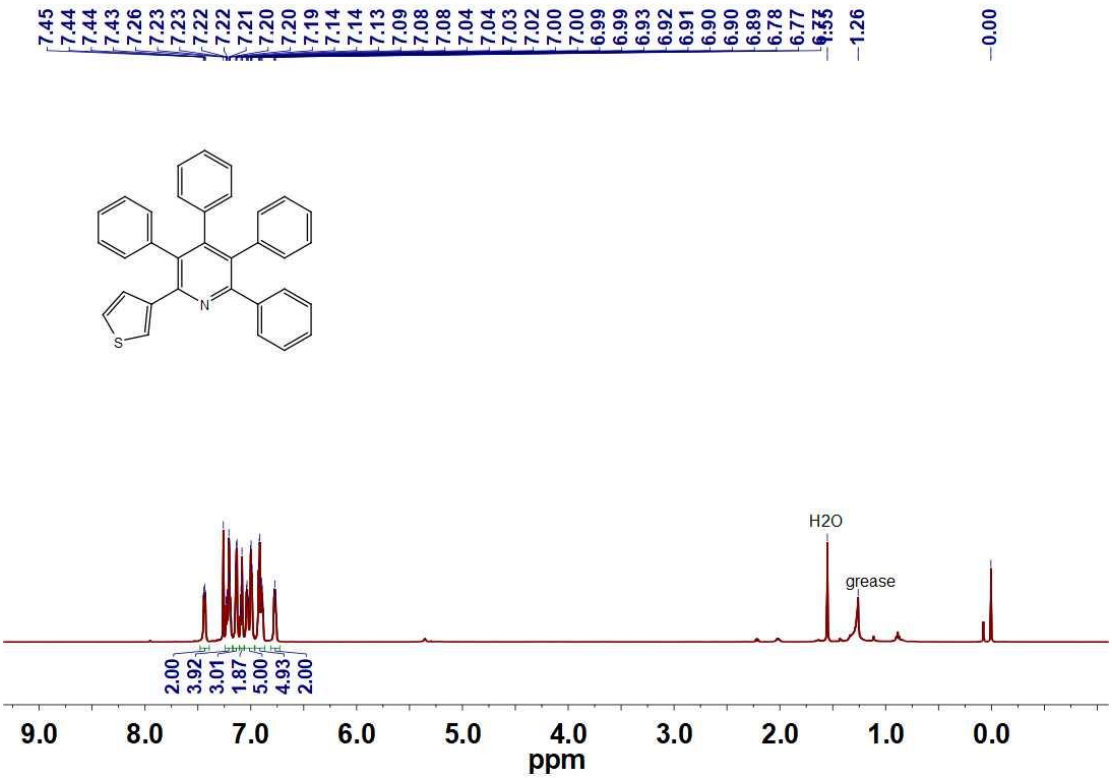


Figure S36. ^{1}H NMR spectrum of **6h** in $CDCl_3$

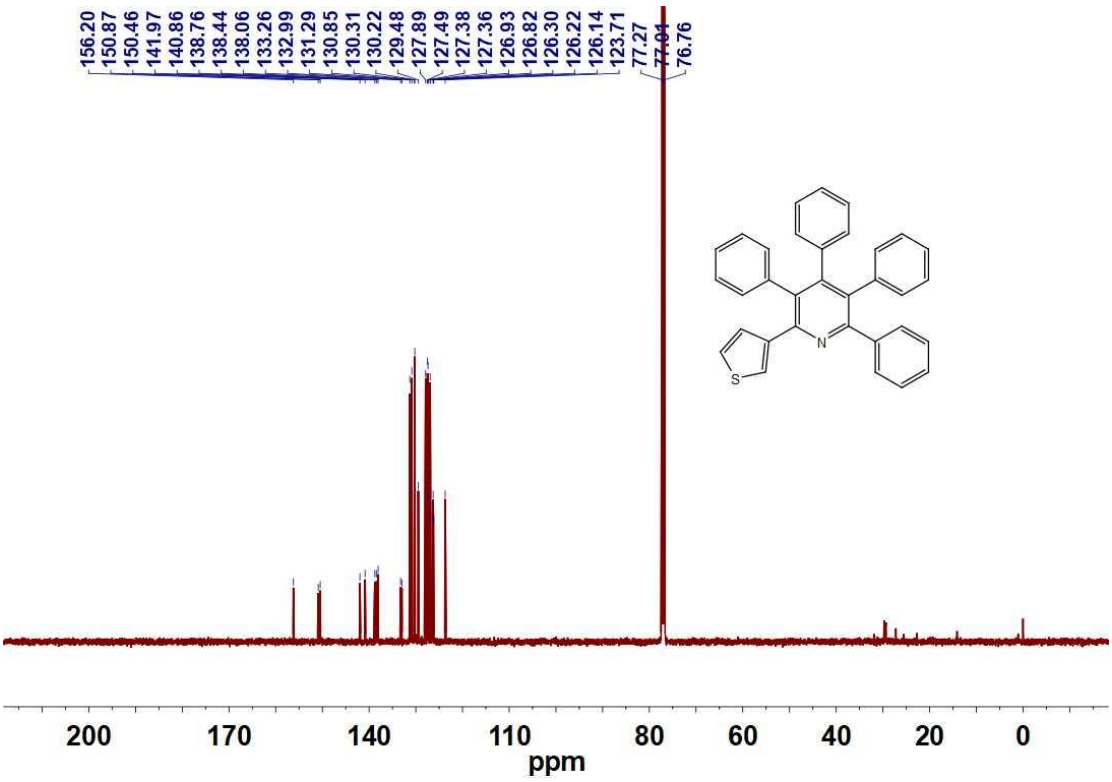


Figure S37. ^{1}H NMR spectrum of **6h** in $CDCl_3$

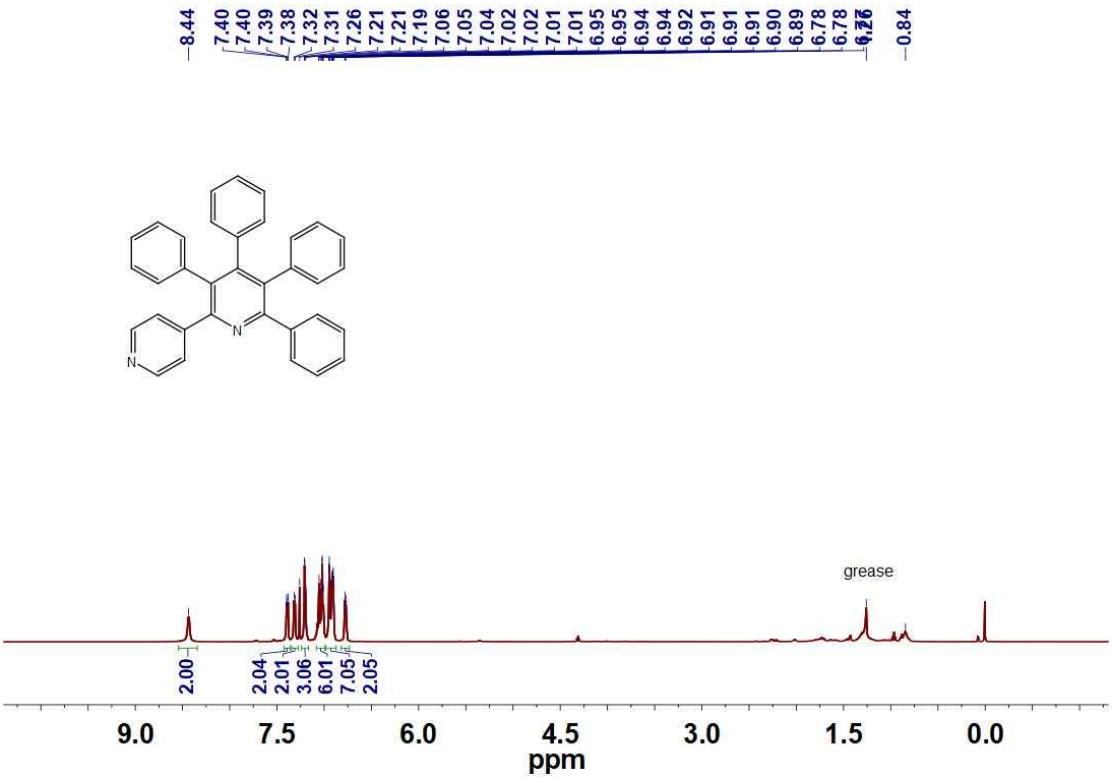


Figure S38. ^{1}H NMR spectrum of **6i** in $CDCl_3$

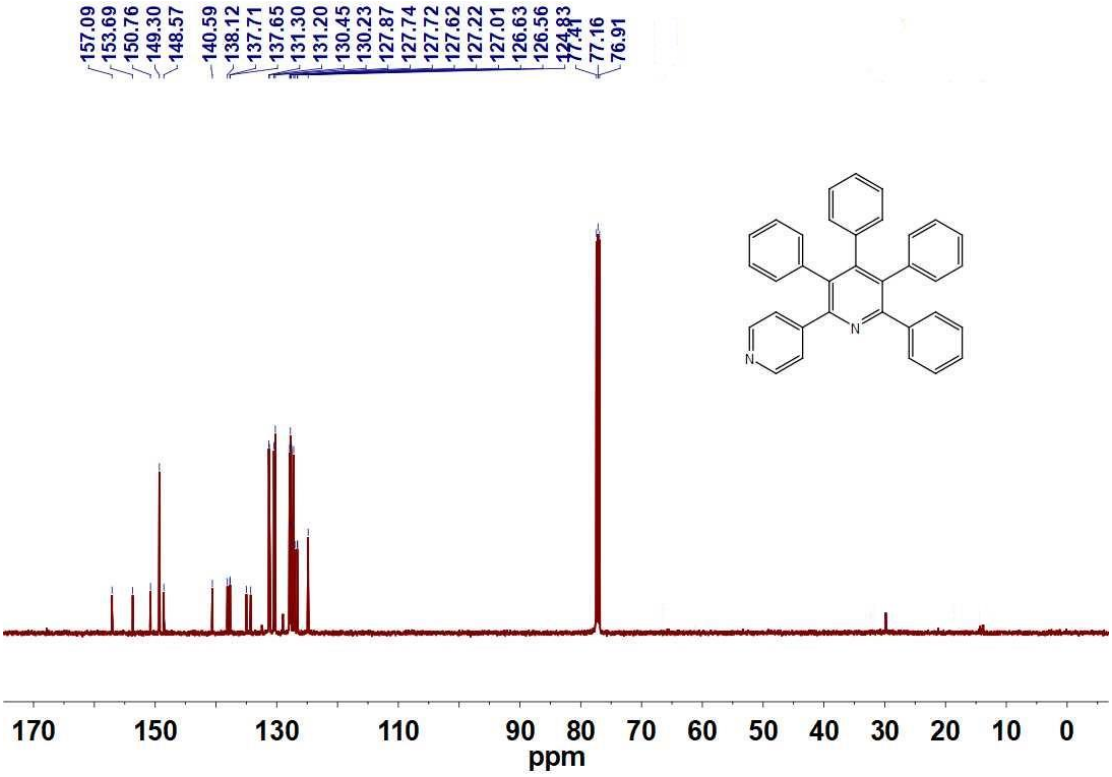


Figure S39. ^{13}C NMR spectrum of **6i** in $CDCl_3$

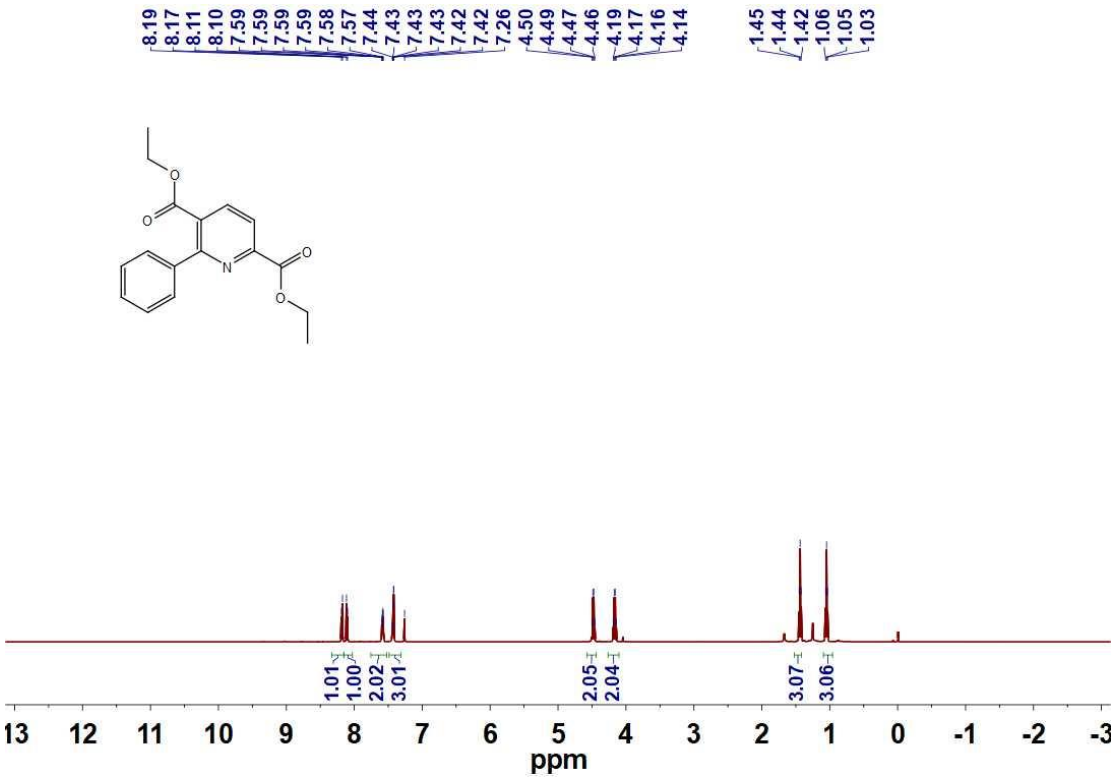


Figure S40. ^{1}H NMR spectrum of **7a** in $CDCl_3$

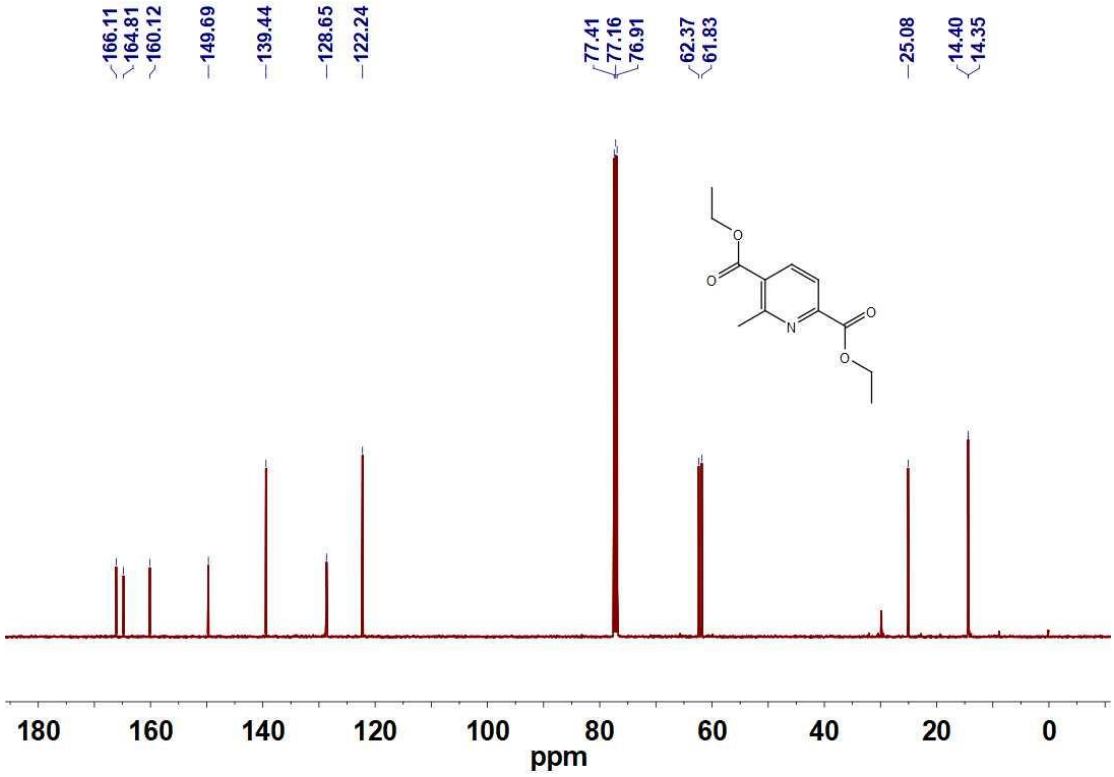


Figure S41. ^{13}C NMR spectrum of **7a** in $CDCl_3$

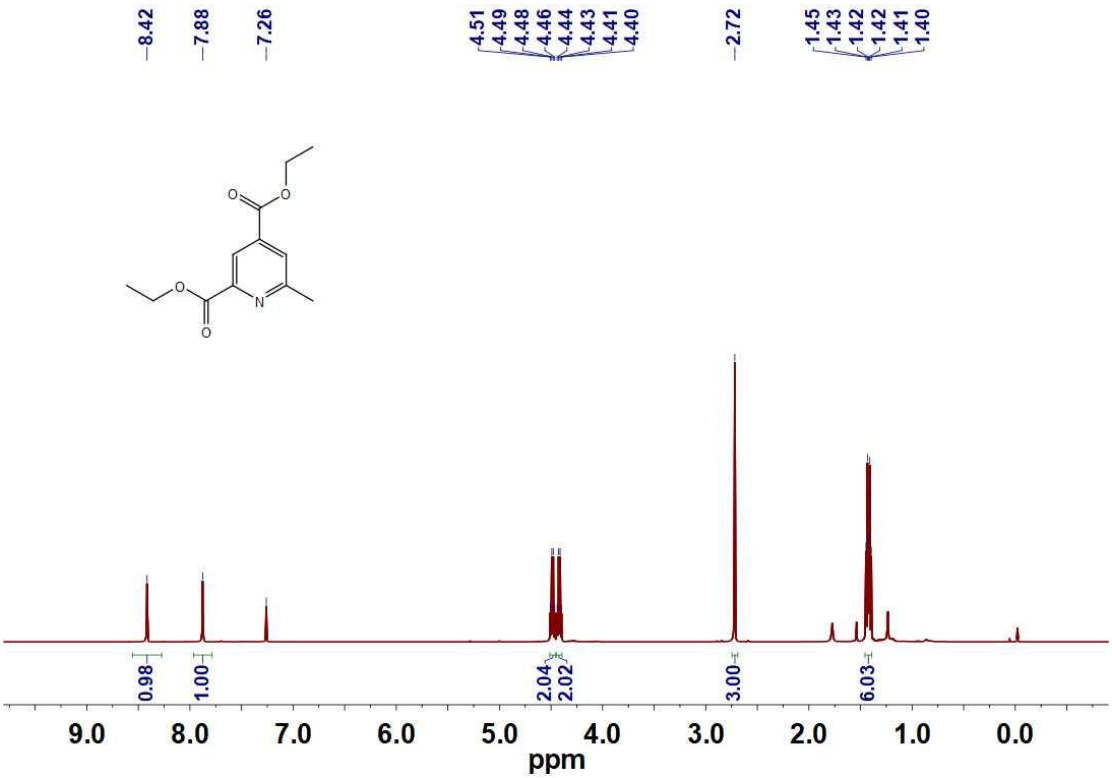


Figure S42. ^{1}H NMR spectrum of **8a** in $CDCl_3$

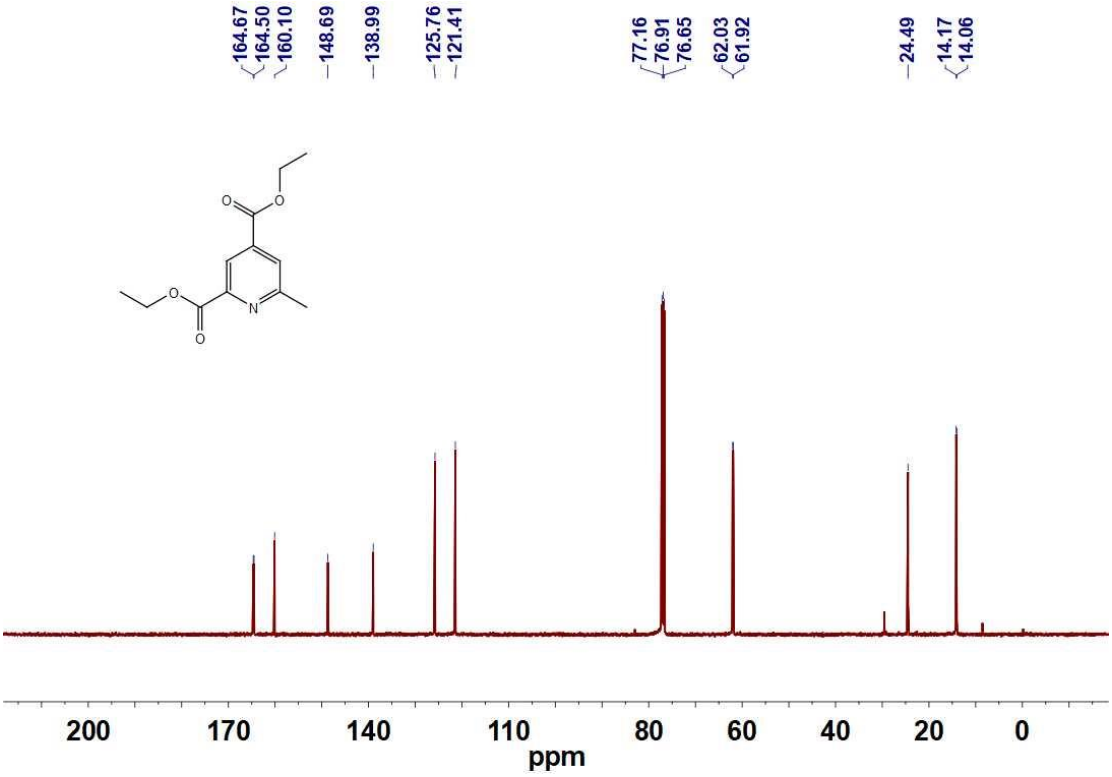


Figure S43. ^{13}C NMR spectrum of **8a** in $CDCl_3$

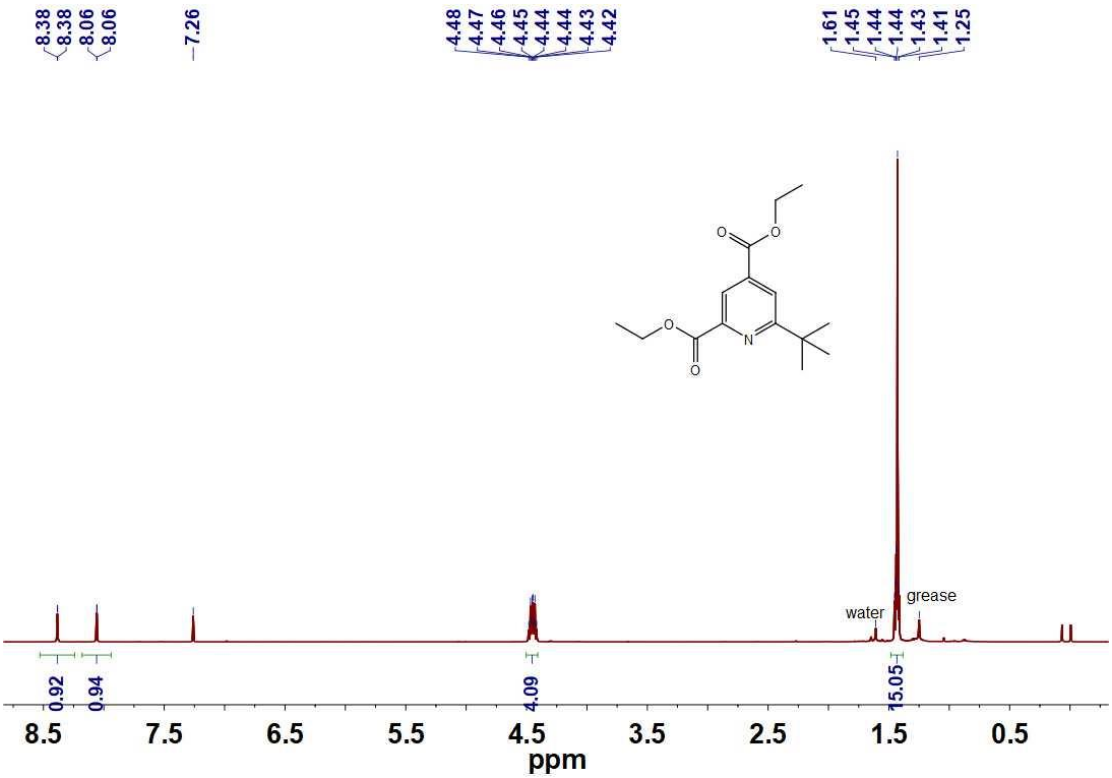


Figure S44. ^{1}H NMR spectrum of **8b** in $CDCl_3$

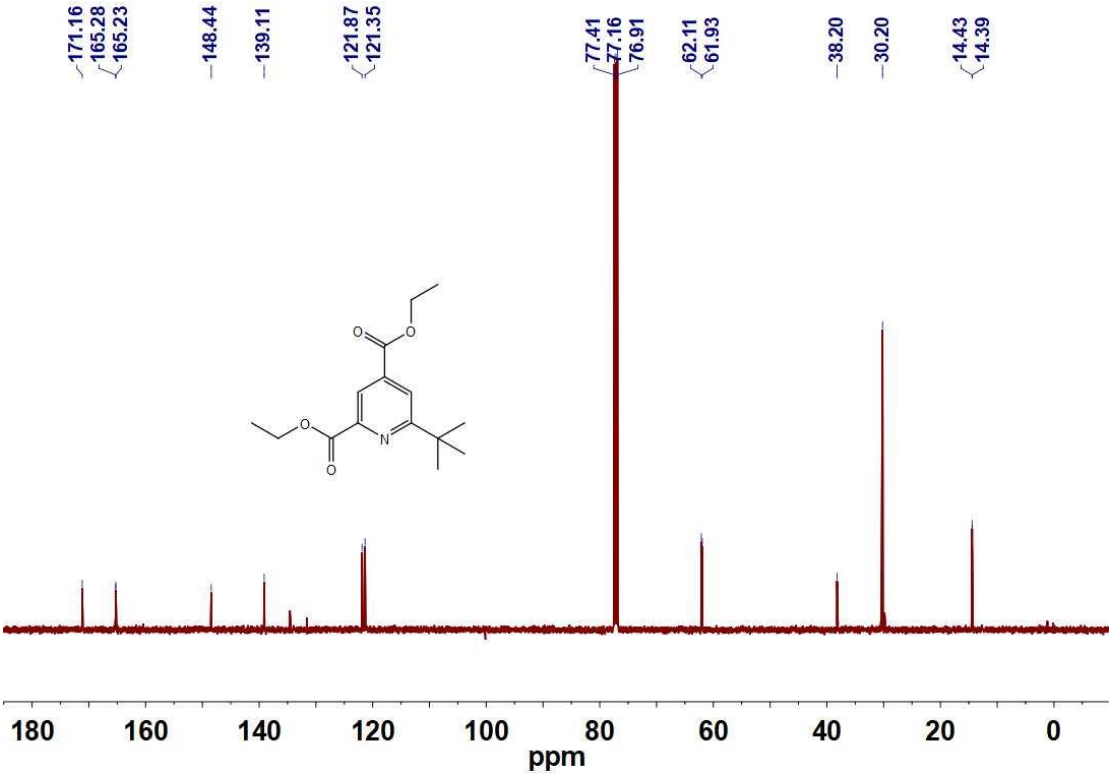


Figure S45. ^{13}C NMR spectrum of **8b** in $CDCl_3$

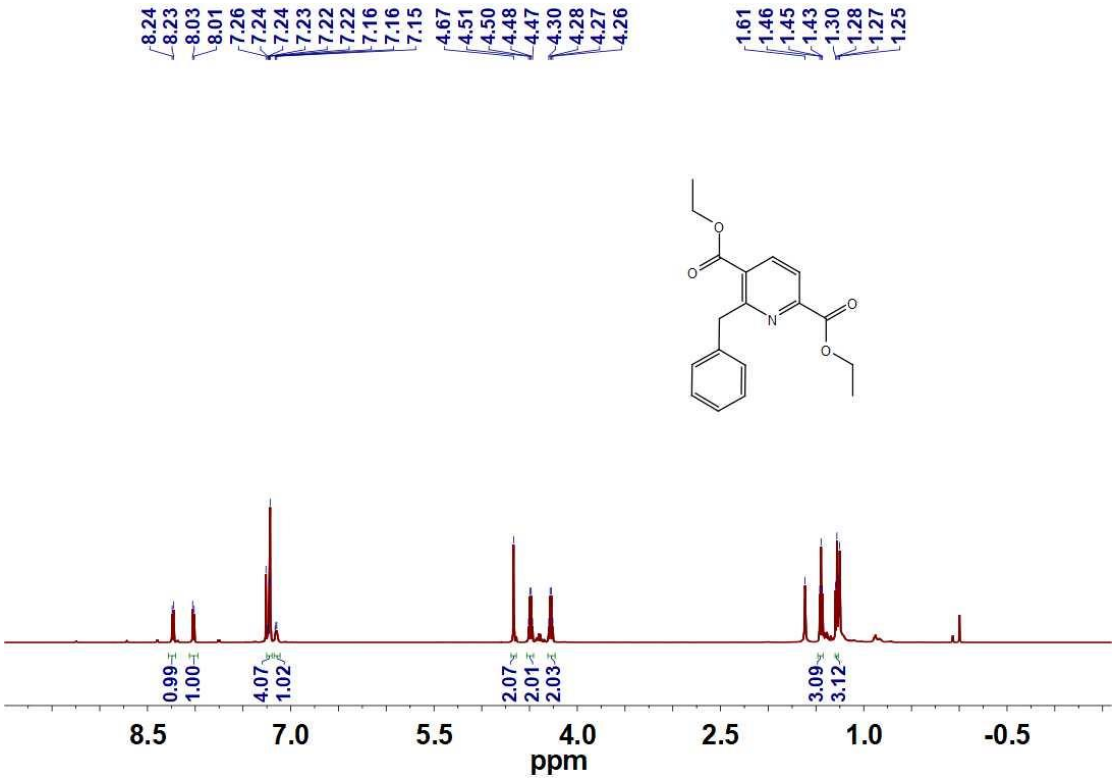


Figure S46. ^{1}H NMR spectrum of **7c** in $CDCl_3$

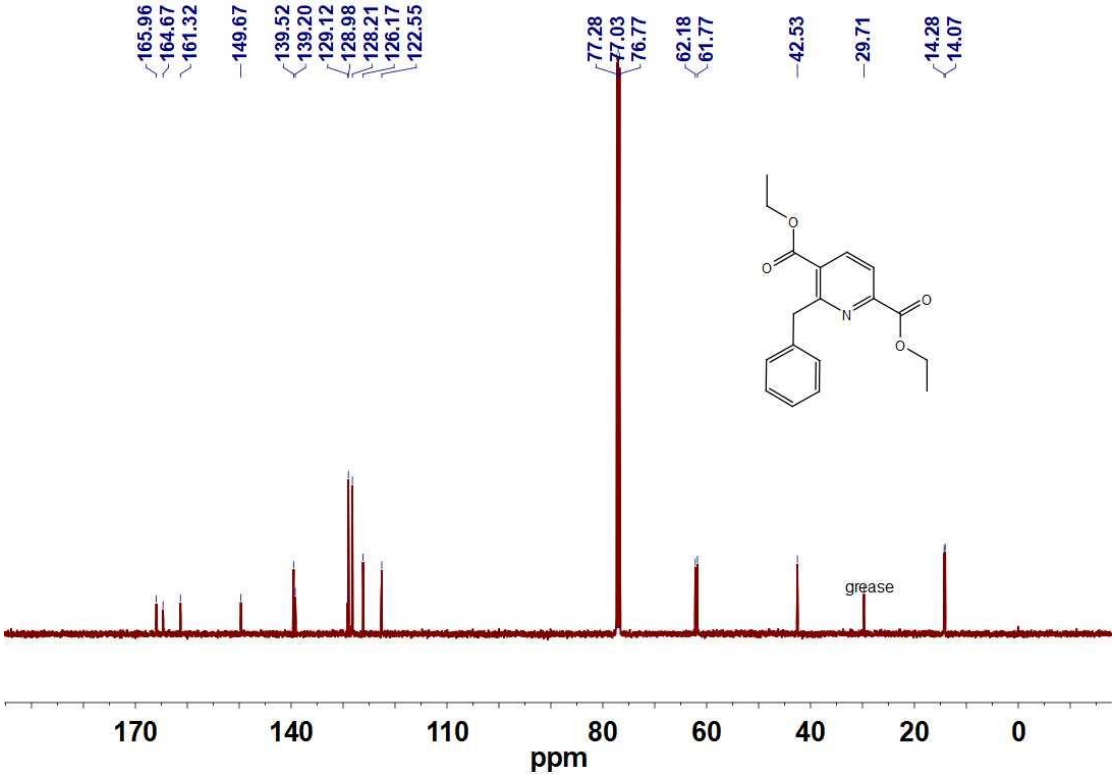


Figure S47. ^{13}C NMR spectrum of **7c** in $CDCl_3$

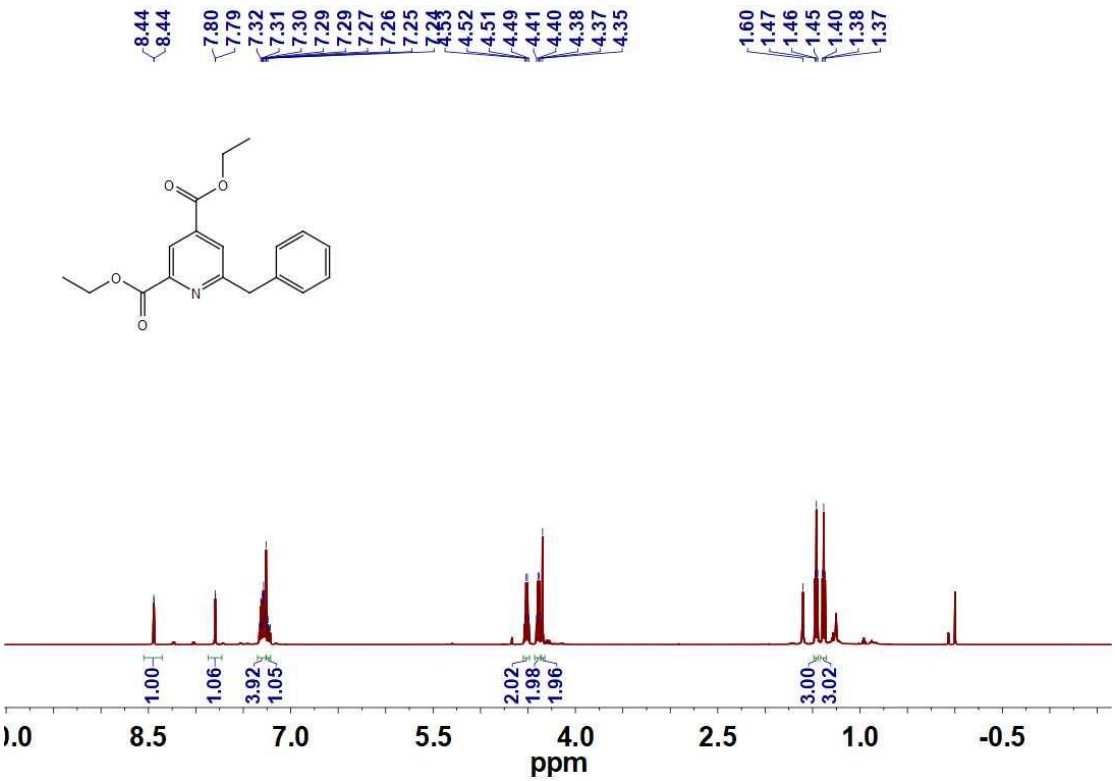


Figure S48. ^{1}H NMR spectrum of **8c** in $CDCl_3$

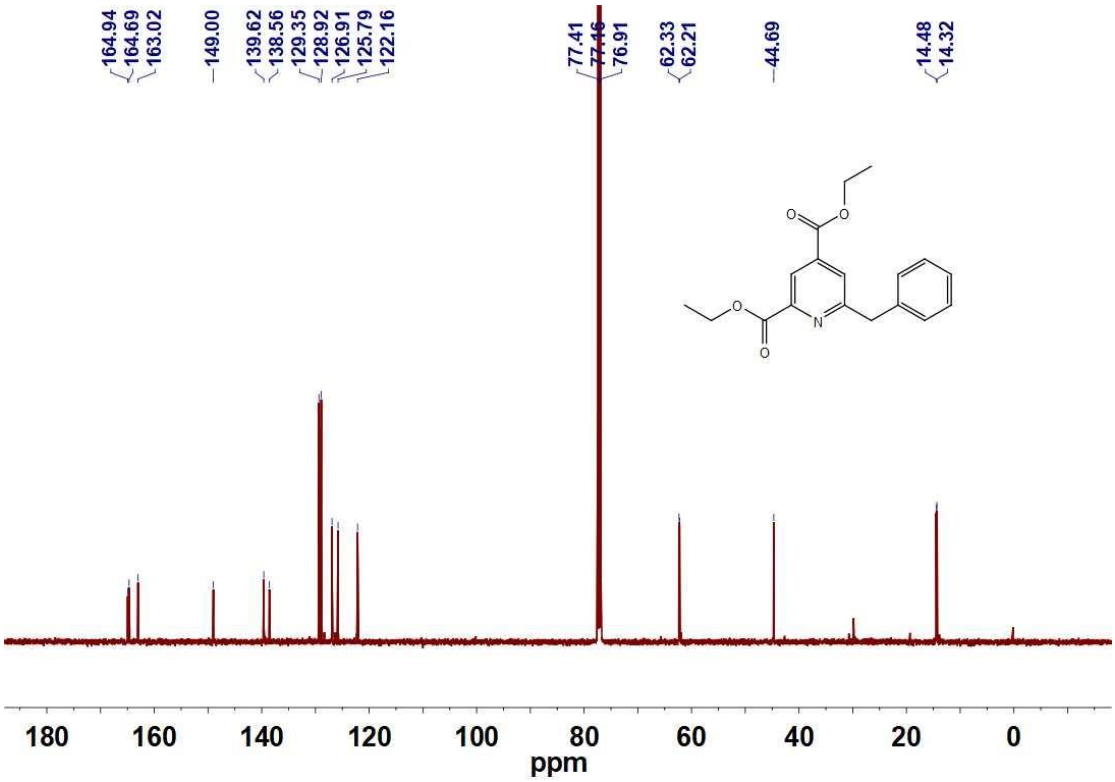


Figure S49. ^{13}C NMR spectrum of **8c** in $CDCl_3$

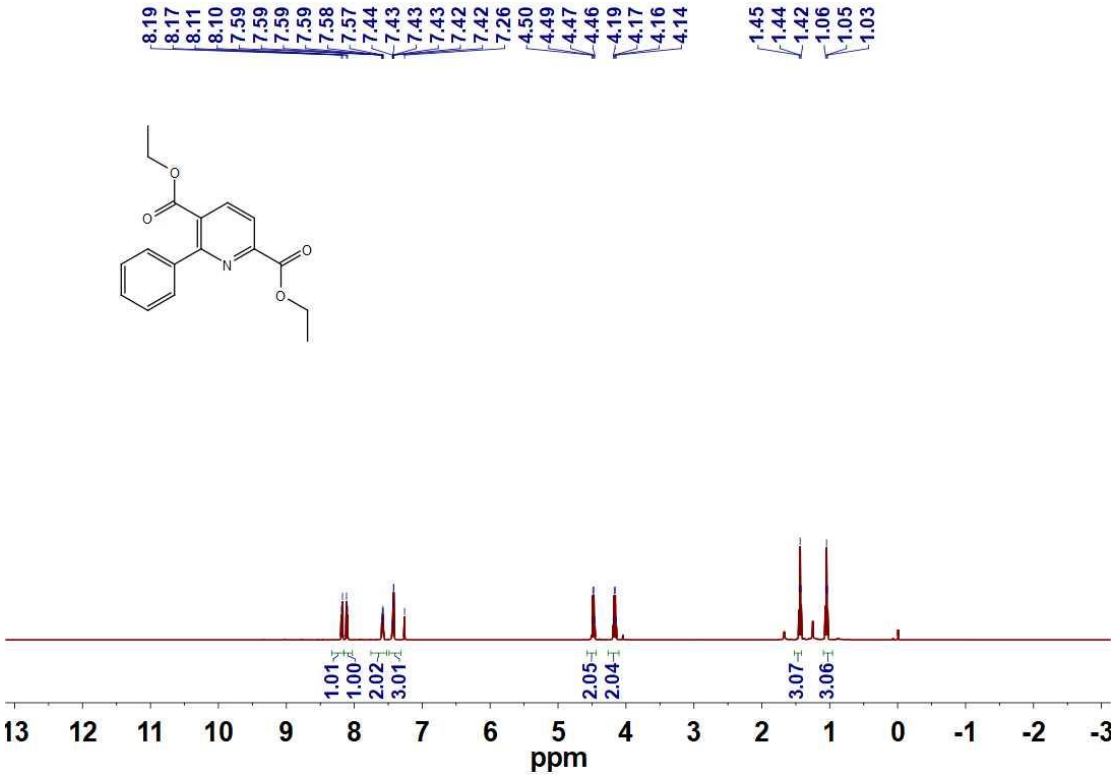


Figure S50. ^{1}H NMR spectrum of **7d** in $CDCl_3$

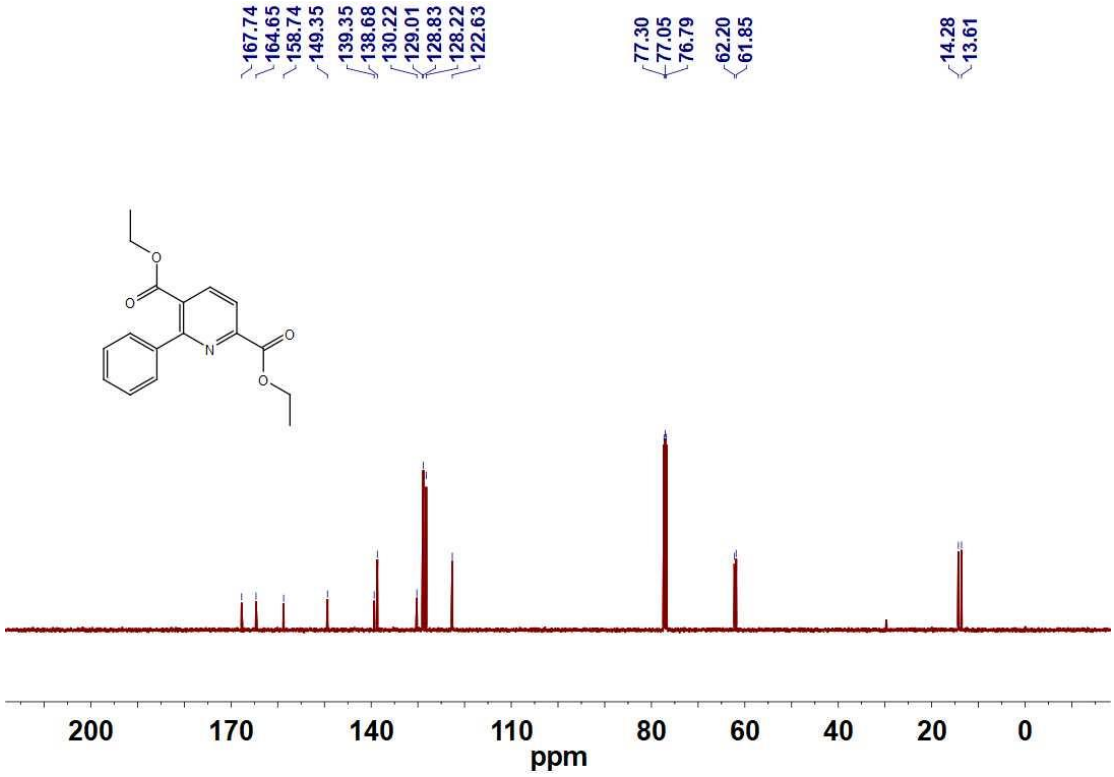


Figure S51. ^{13}C NMR spectrum of **7d** in $CDCl_3$

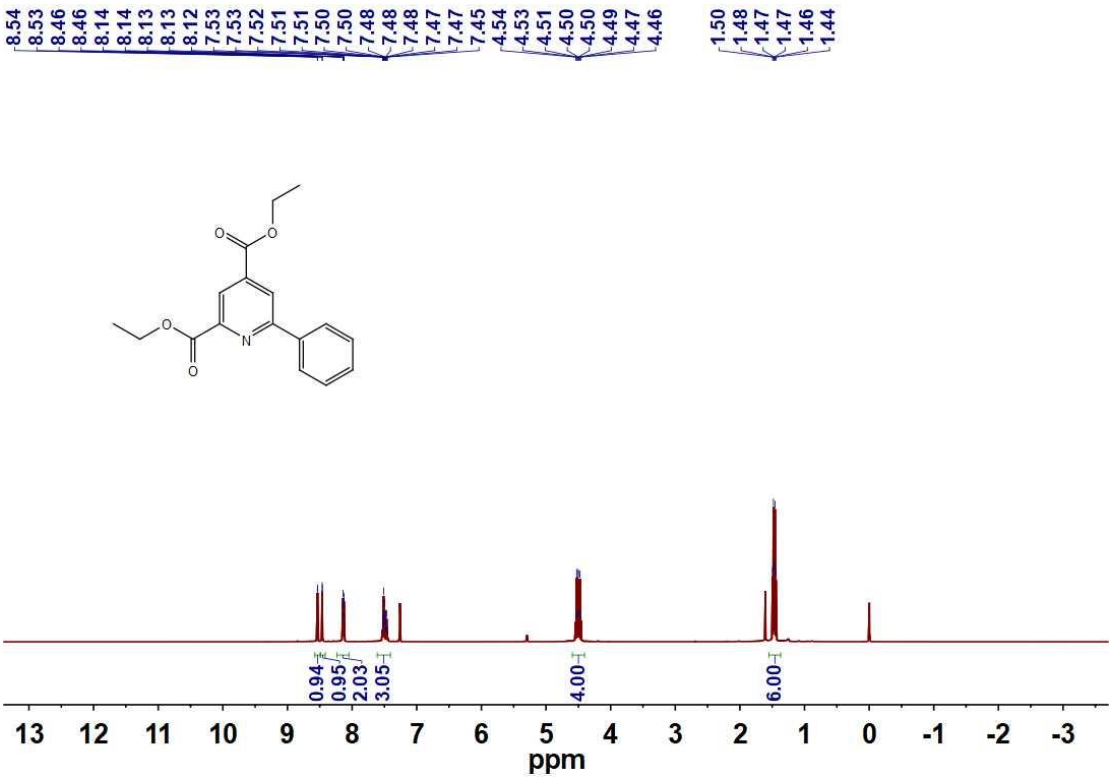


Figure S52. ^{1}H NMR spectrum of **8d** in $CDCl_3$

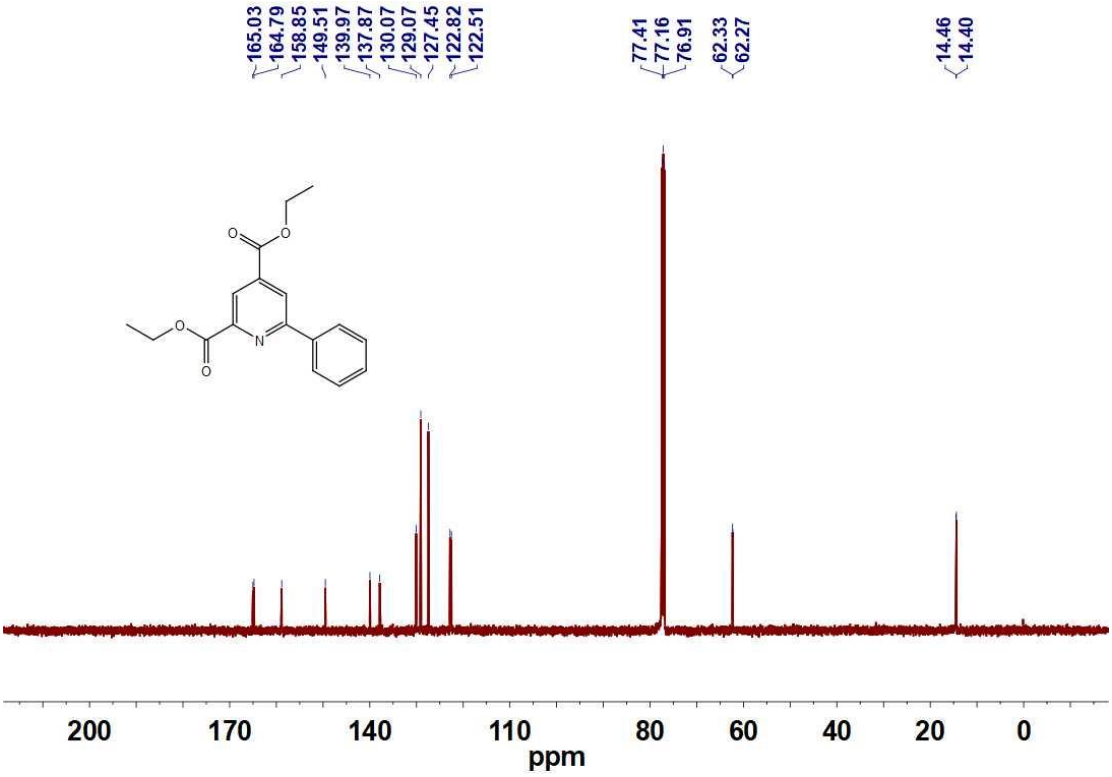


Figure S53. ^{13}C NMR spectrum of **8d** in $CDCl_3$

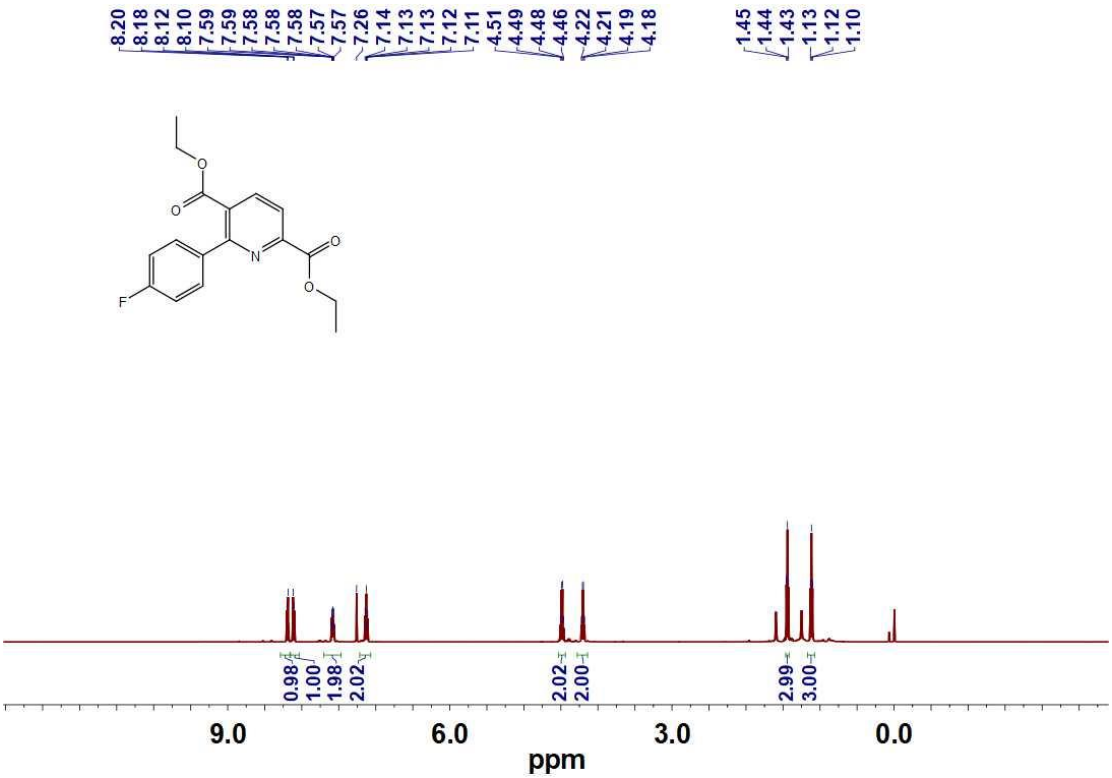


Figure S54. ^{1}H NMR spectrum of **7e** in $CDCl_3$

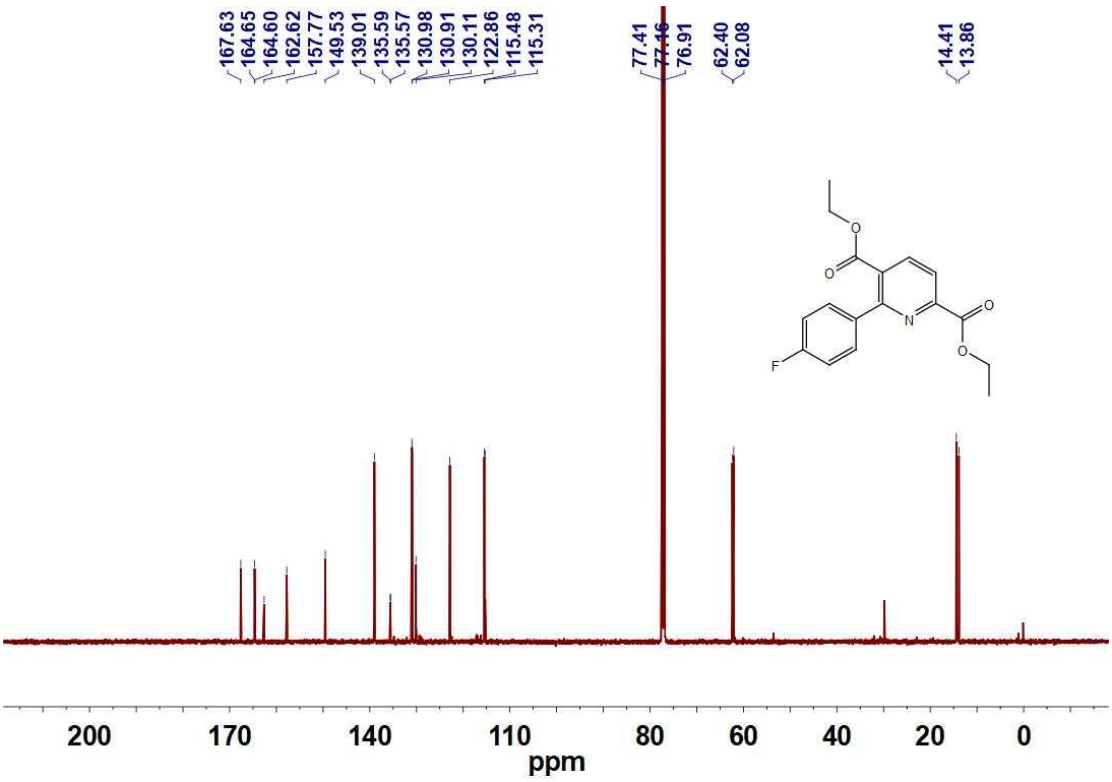


Figure S55. ^{13}C NMR spectrum of **7e** in $CDCl_3$

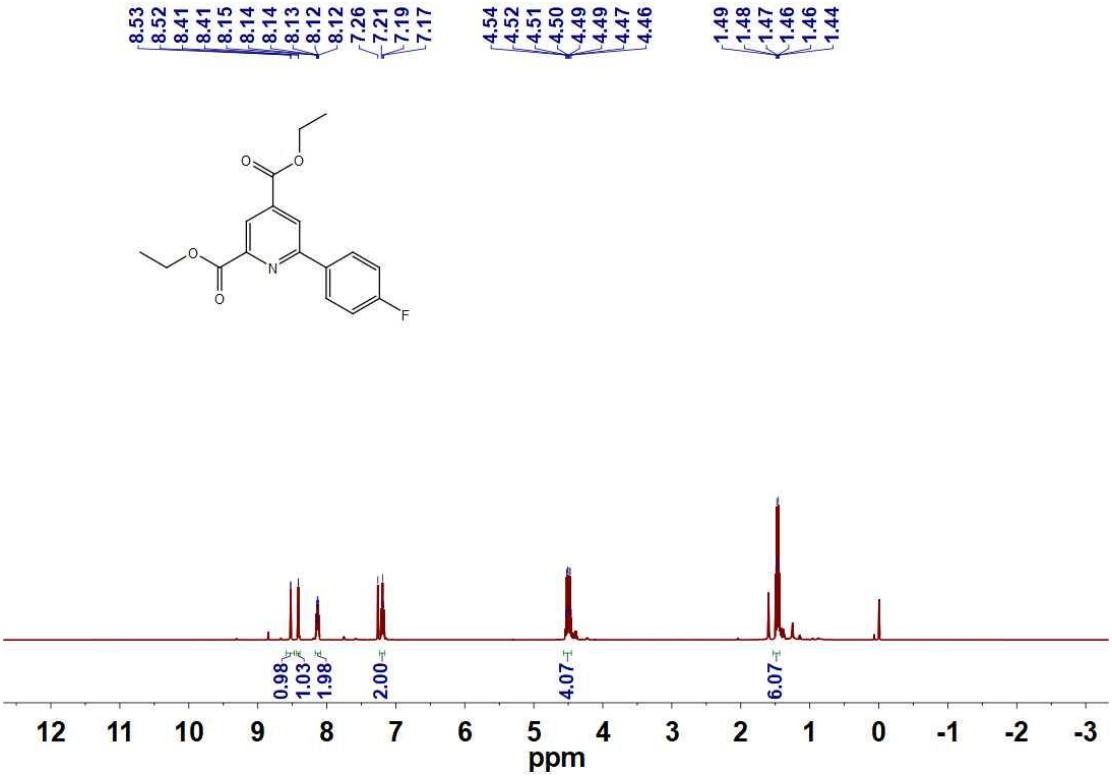


Figure S56. ^{1}H NMR spectrum of **8e** in $CDCl_3$

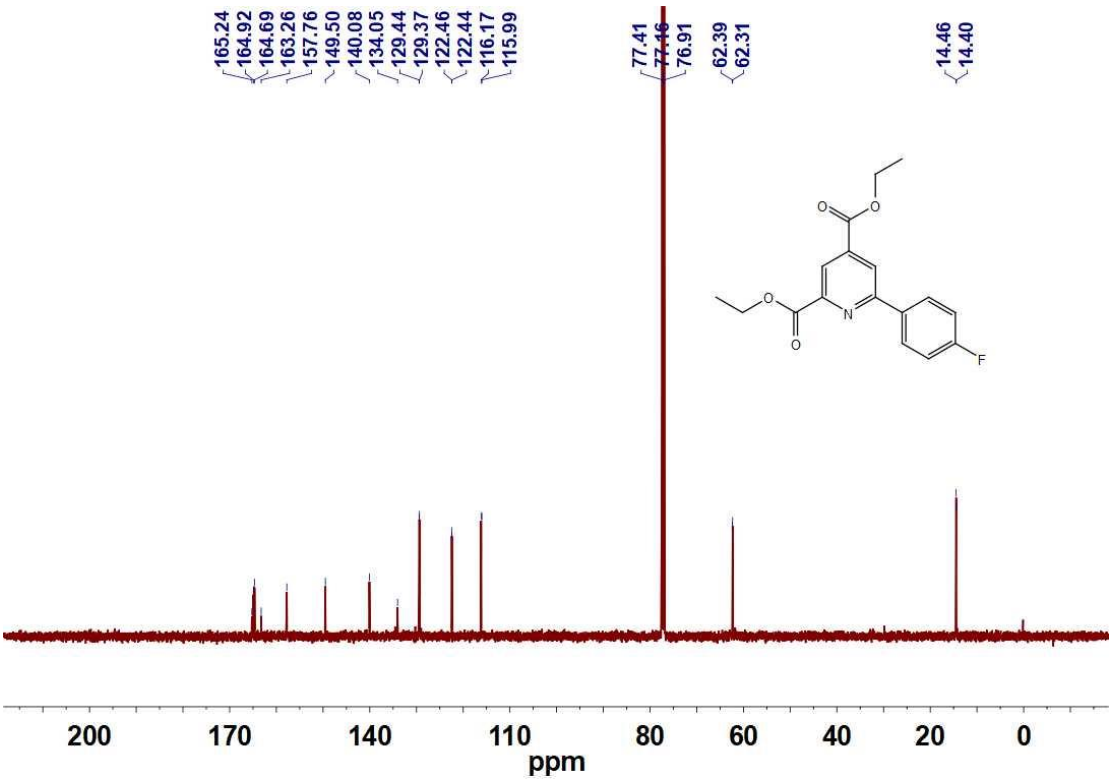


Figure S57. ^{13}C NMR spectrum of **8e** in $CDCl_3$

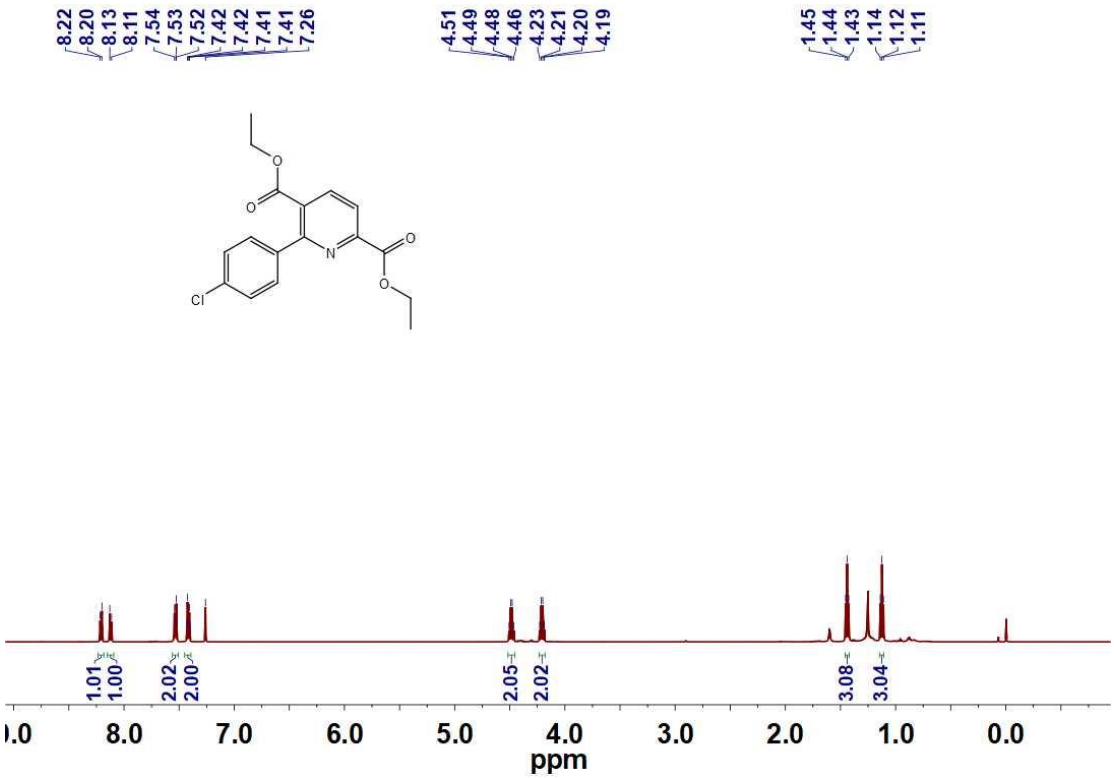


Figure S58. ^{1}H NMR spectrum of **7f** in $CDCl_3$

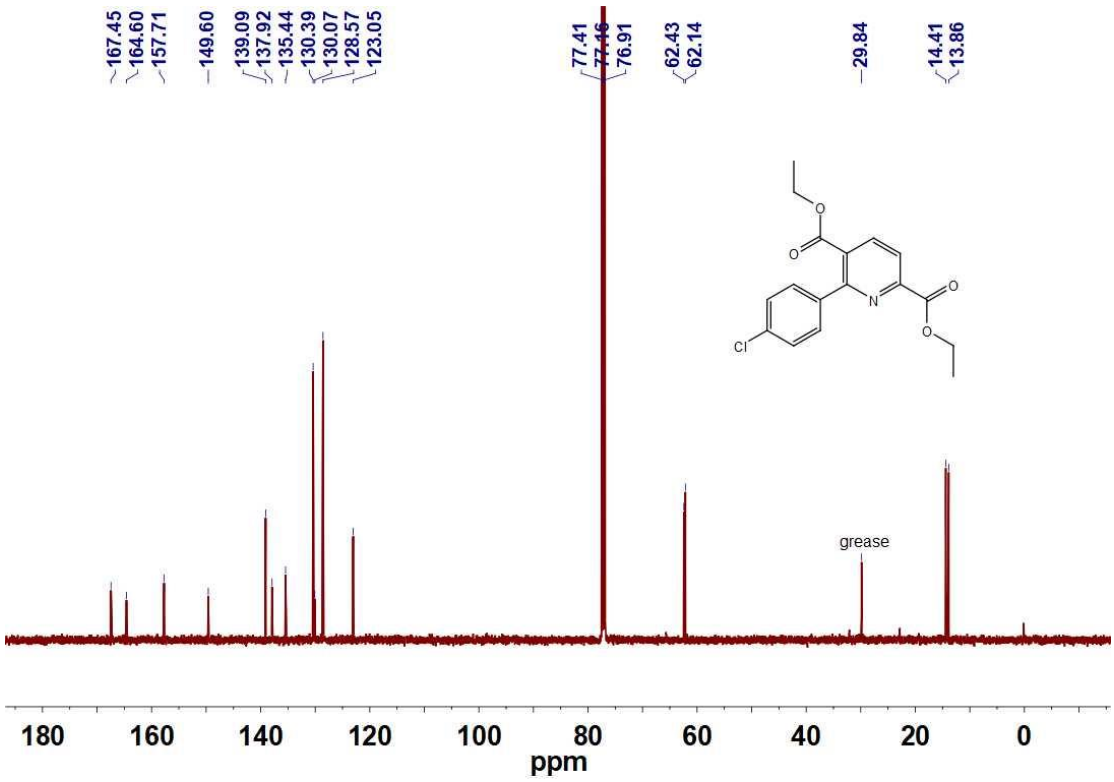


Figure S59. ^{13}C NMR spectrum of **7f** in $CDCl_3$

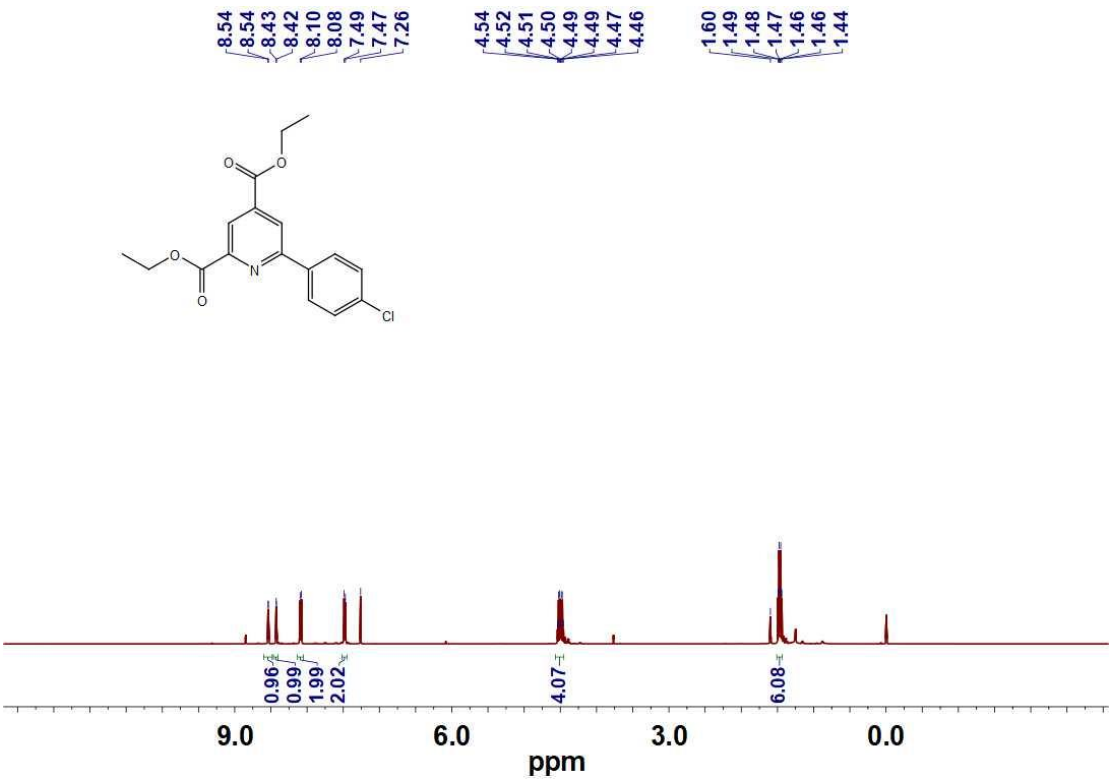


Figure S60. ^{1}H NMR spectrum of **8f** in $CDCl_3$

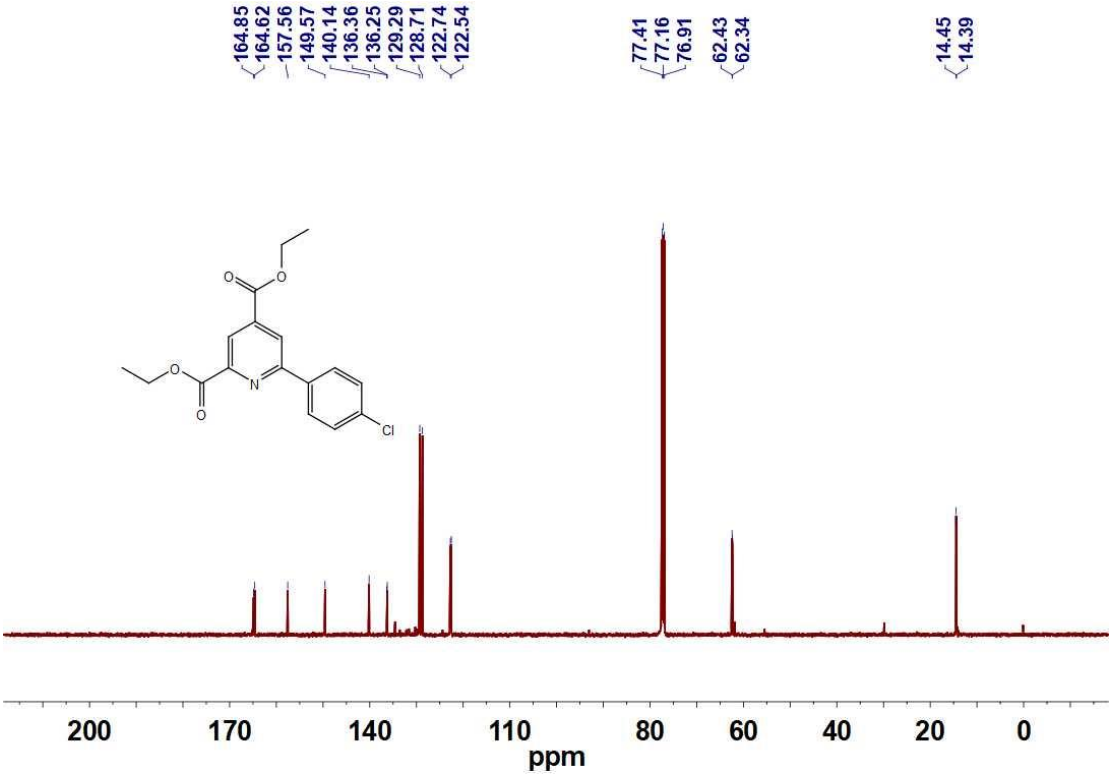


Figure S61. ^{13}C NMR spectrum of **8f** in $CDCl_3$

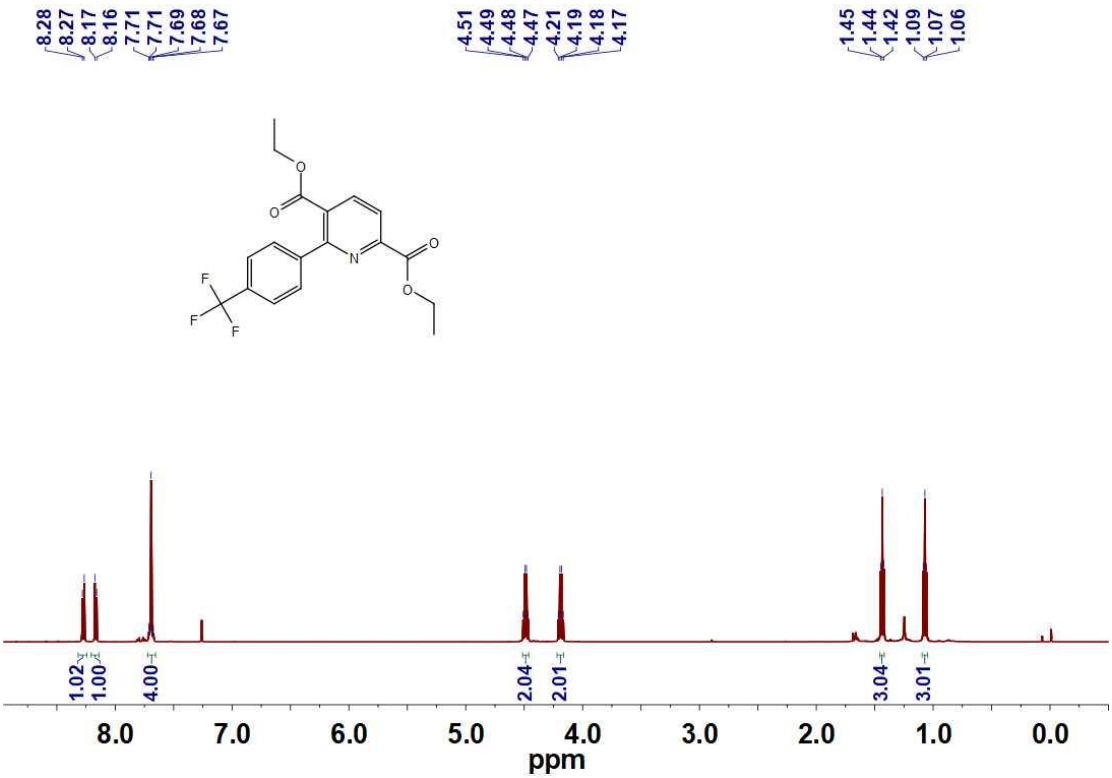


Figure S62. ^{1}H NMR spectrum of **7g** in $CDCl_3$

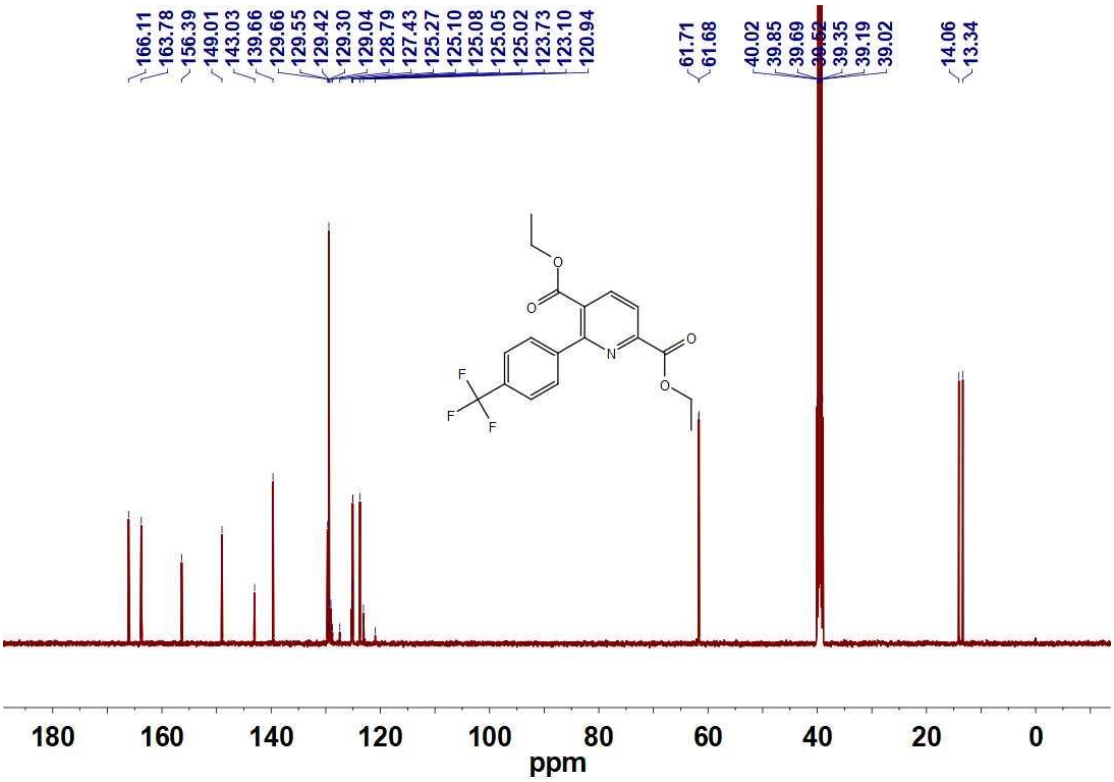


Figure S63. ^{13}C NMR spectrum of **7g** in DMSO-d_6

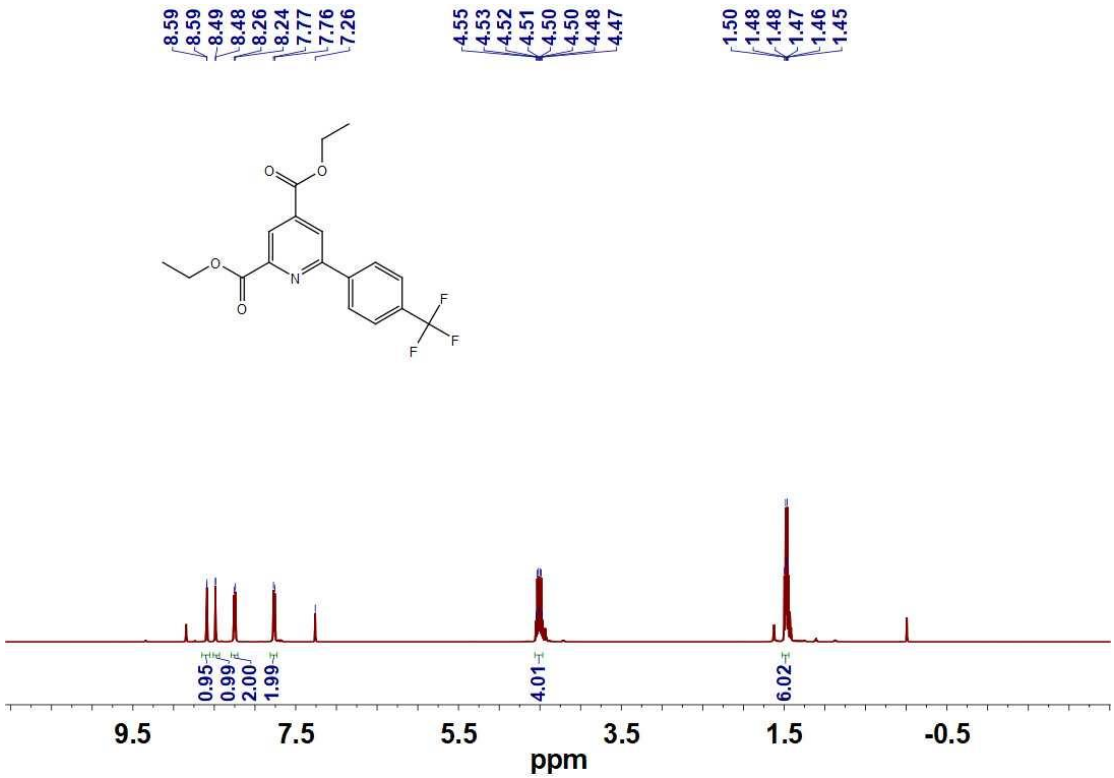


Figure S64. ^{1}H NMR spectrum of **8g** in $CDCl_3$

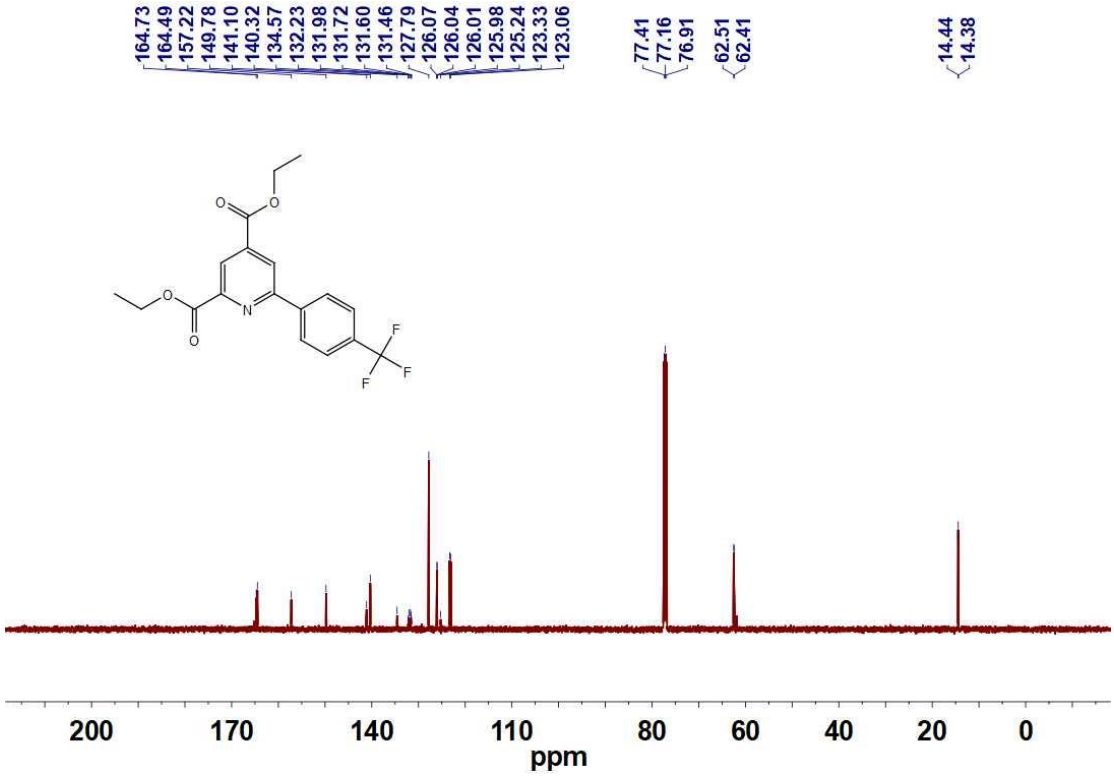


Figure S65. ^{13}C NMR spectrum of **8g** in $CDCl_3$

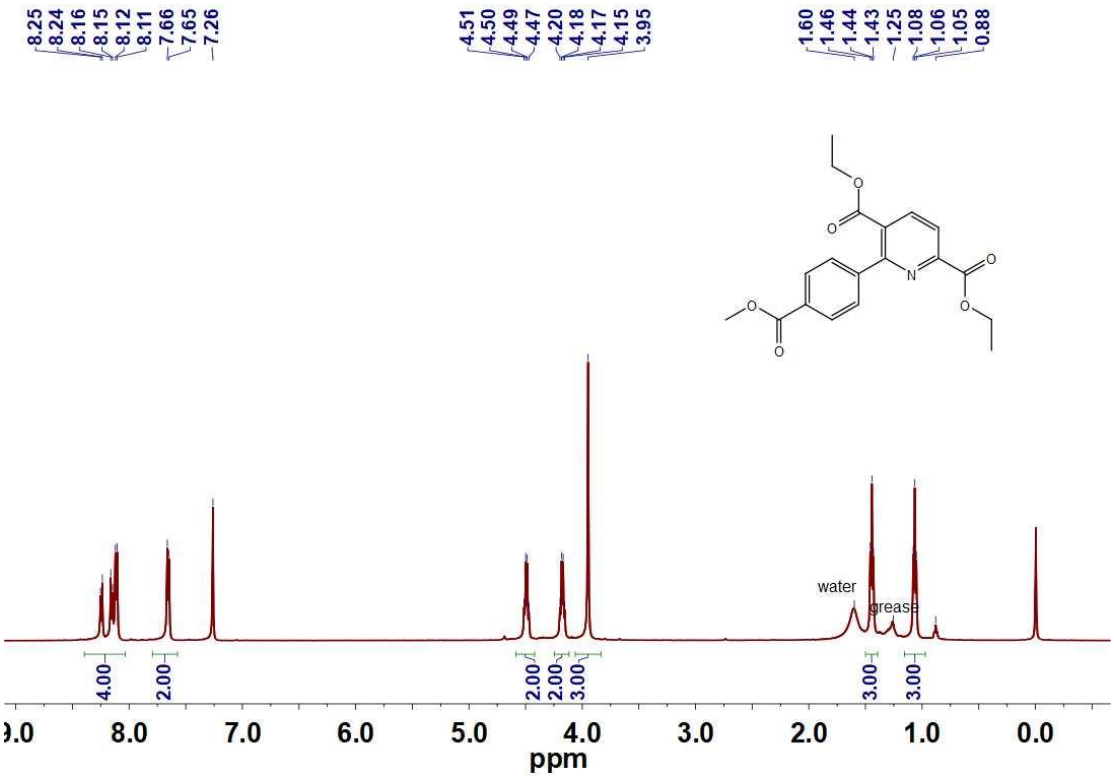


Figure S66. ^{1}H NMR spectrum of **7h** in $CDCl_3$

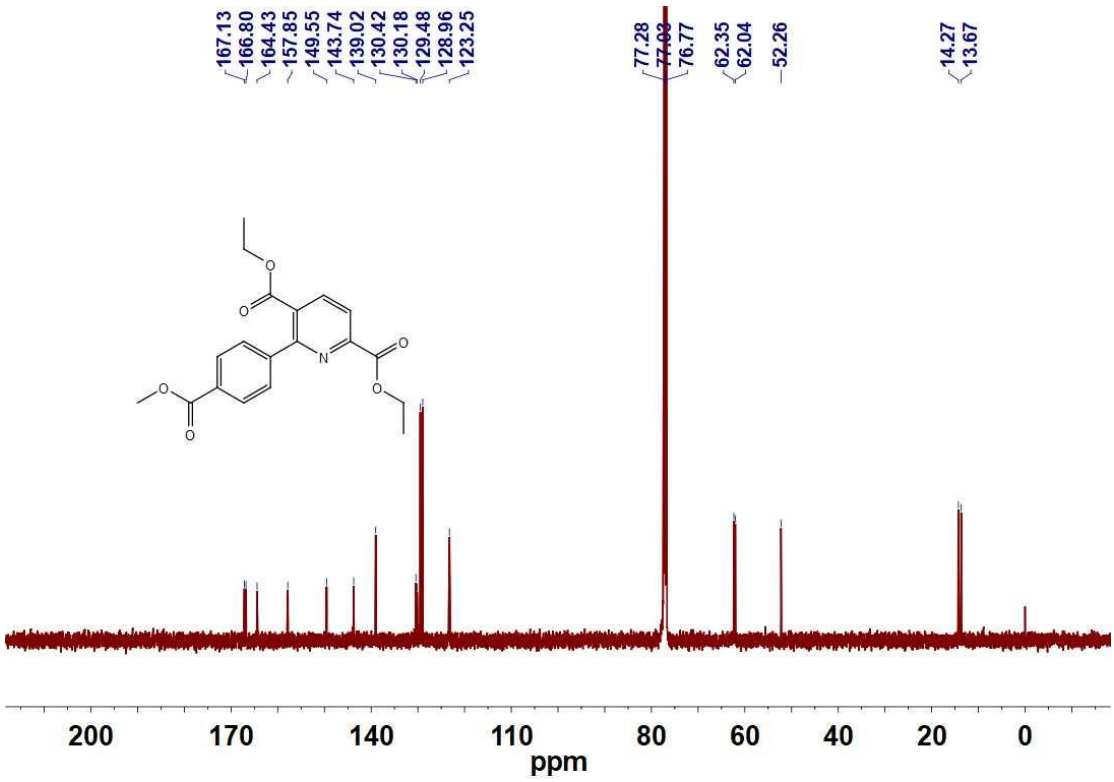


Figure S67. ^{13}C NMR spectrum of **7h** in $CDCl_3$

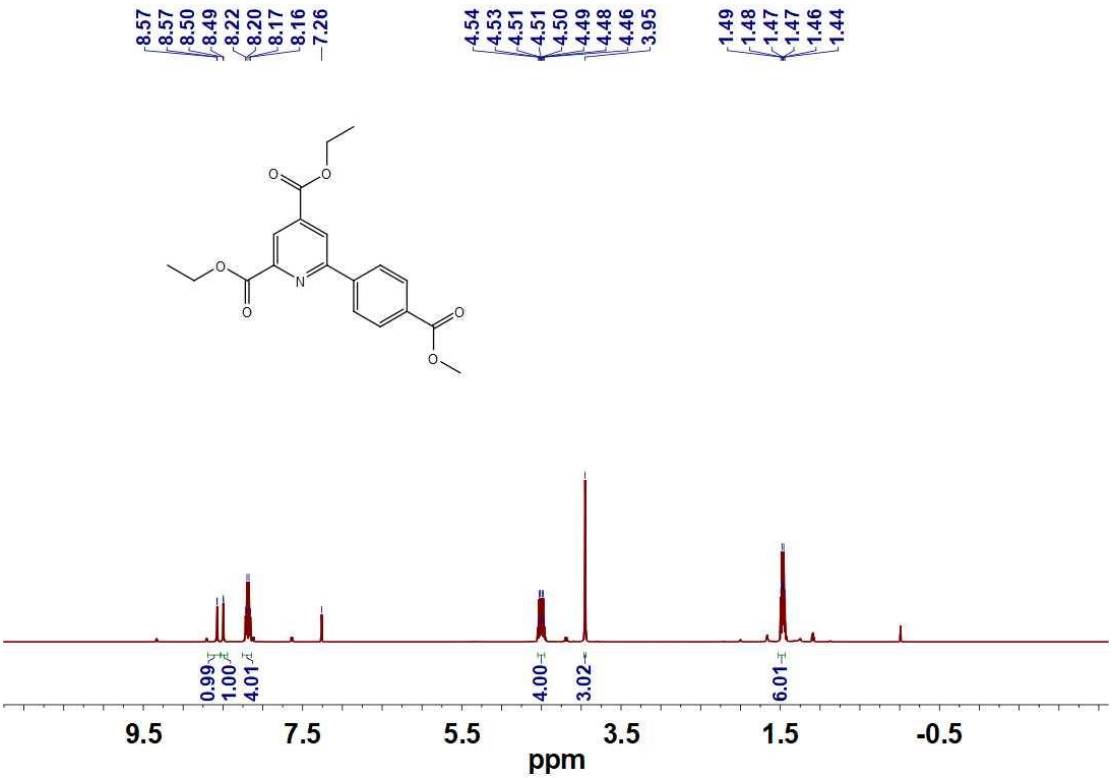


Figure S68. ^{1}H NMR spectrum of **8h** in $CDCl_3$

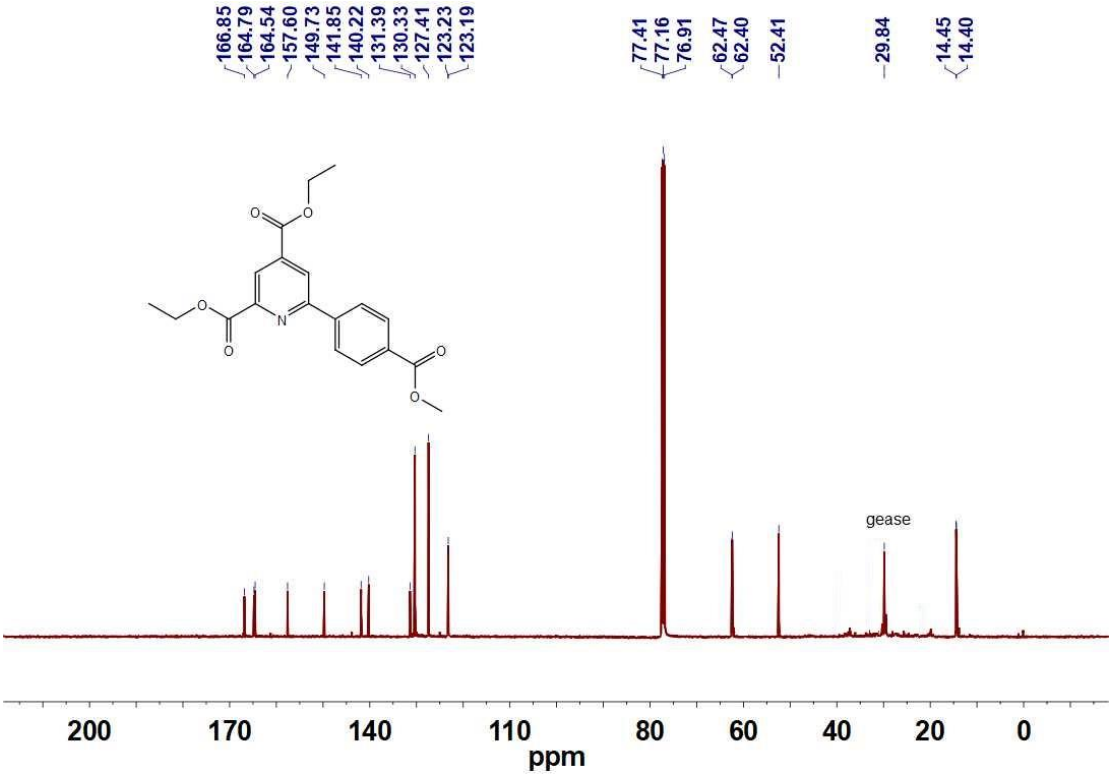


Figure S69. ^{13}C NMR spectrum of **8h** in $CDCl_3$

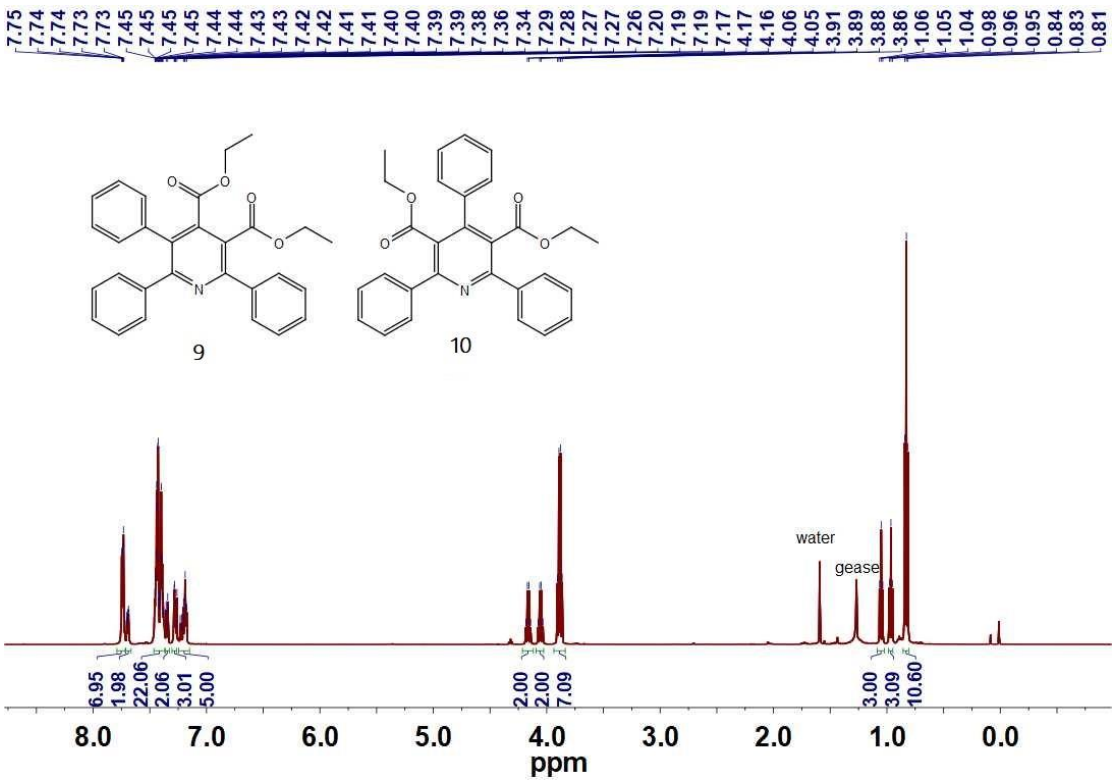


Figure S70. ^{1}H NMR spectrum of **9** and **10** in $CDCl_3$

5. Crystal data and structure refinement parameters

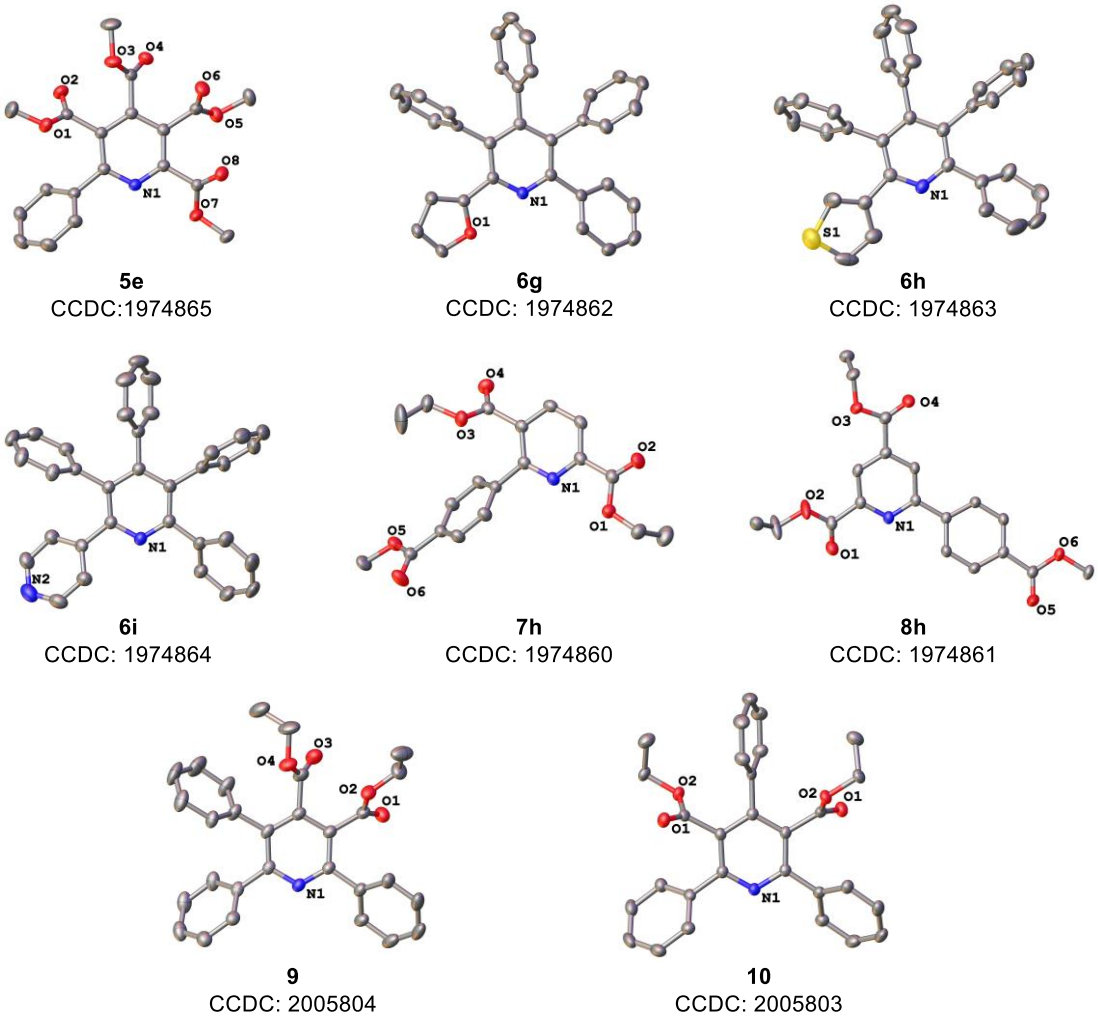


Figure S71. X-ray structure of **5e**, **6g-6i**, **7h**, **8h**, **9** and **10** showing 50% probability ellipsoids. For clarity, hydrogen atoms are omitted.

Table S2. Crystal data and structure refinement for **5e**, **6g** and **6h**.

Identification code	**5e**	**6g**	**6h**
Empirical formula	$C_{19}H_{17}NO_8$	$C_{33}H_{23}NO$	$C_{33}H_{23}NS$
Formula weight	387.33	449.52	465.58
Temperature/K	172.99(10)	172.99(10)	172.97(10)
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	P-1
a/Å	8.3982(2)	9.9189(5)	9.4561(4)
b/Å	9.2747(2)	10.1839(4)	10.7759(5)
c/Å	12.2174(3)	12.4921(5)	12.6690(4)
α/°	97.153(2)	77.403(4)	74.816(3)
β/°	91.869(2)	89.399(4)	87.896(3)
γ/°	95.266(2)	77.392(4)	82.262(4)
Volume/Å^3	939.30(4)	1200.88(9)	1234.53(9)
Z	2	2	2
Density (calculated) (g/cm^3)	1.37	1.243	1.252
Absorption coefficient (mm^{-1})	0.921	0.576	1.316
F(000)	404	472	488
Radiation	Cu*K*α (λ = 1.54184)	Cu*K*α (λ = 1.54184)	CuKα (λ = 1.54184)
Crystal color, morphology	Colorless, block	Colorless, block	Colorless, block
2θ range (°)	7.3 to 134.16	9.124 to 134.144	7.23 to 134.12
Absorption correction	Multi-scan	Multi-scan	Multi-scan
T_{min}, T_{max}	0.097, 1.000	0.752, 1.000	0.777, 1.000
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 8, -14 ≤ l ≤ 14	-11 ≤ h ≤ 10, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14	-9 ≤ h ≤ 11, -12 ≤ k ≤ 12, -15 ≤ l ≤ 14
Reflections collected	7821	10933	11884
Independent reflections	3295 [R_{int} = 0.0336, R_{sigma} = 0.0306]	4211 [R_{int} = 0.0346, R_{sigma} = 0.0390]	4347 [R_{int} = 0.0370, R_{sigma} = 0.0392]
Goodness-of-fit on F2	1.097	1.033	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0460, wR_2 = 0.1248	R_1 = 0.0382, wR_2 = 0.0942	R_1 = 0.0956, wR_2 = 0.2480
Final R indexes [all data]	R_1 = 0.0544, wR_2 = 0.1504	R_1 = 0.0470, wR_2 = 0.1024	R_1 = 0.1069, wR_2 = 0.2612
Largest diff. peak/hole / e Å^{-3}	0.29/-0.32	0.14/-0.20	0.73/-1.19

Table S3. Crystal data and structure refinement for **6i**, **7g** and **8h**.

Identification code	**6i**	**7h**	**8h**
Empirical formula	$C_{34}H_{24}N_2$	$C_{19}H_{19}NO_6$	$C_{19}H_{19}NO_6$
Formula weight	459.56	357.35	357.37
Temperature/K	170.00(10)	172.99(10)	172.99(10)
Crystal system	triclinic	triclinic	monoclinic
Space group	*P*-1	*P*-1	*P21*/c
a/Å	9.4955(3)	6.1349(3)	8.0143(2)
b/Å	10.7087(3)	9.9549(6)	16.4743(5)
c/Å	12.7175(3)	15.8859(9)	12.9122(3)
α/°	75.731(2)	75.901(5)	90
β/°	87.433(3)	82.885(5)	93.475(2)
γ/°	82.570(3)	78.777(5)	90
Volume/Å^3	1242.64(6)	919.98(9)	1701.66(8)
Z	2	2	4
Density (calculated) (g/cm^3)	1.228	1.29	1.3948
Absorption coefficient (mm^{-1})	0.537	0.808	0.874
F(000)	484	376	754.7
Radiation	Cu*K*α (λ = 1.54184)	Cu*K*α (λ = 1.54184)	Cu*K*α (λ = 1.54184)
Crystal color, morphology	Colorless, block	Colorless, block	Colorless, block
2θ range (°)	8.584 to 134.156	5.754 to 134.152	8.72 to 134.14
Absorption correction	Multi-scan	Multi-scan	Multi-scan
T_{min}, T_{max}	0.763, 1.000	0.704, 1.000	0.712, 1.000
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -15 ≤ l ≤ 8	-7 ≤ h ≤ 6, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18	-9 ≤ h ≤ 10, -7 ≤ k ≤ 20, -16 ≤ l ≤ 15
Reflections collected	11018	8436	10051
Independent reflections	4372 [R_{int} = 0.0233, R_{sigma} = 0.0255]	3233 [R_{int} = 0.0491, R_{sigma} = 0.0484]	3006 [R_{int} = 0.0388, R_{sigma} = 0.0422]
Goodness-of-fit on F2	1.098	1.169	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0448, wR_2 = 0.1077	R_1 = 0.0600, wR_2 = 0.1418	R_1 = 0.0483, wR_2 = 0.1228
Final R indexes [all data]	R_1 = 0.0501, wR_2 = 0.1140	R_1 = 0.0767, wR_2 = 0.1529	R_1 = 0.0624, wR_2 = 0.1354
Largest diff. peak/hole / e Å^{-3}	0.23/-0.23	0.28/-0.27	0.40/-0.50

Table S4. Crystal data and structure refinement for **9**, **10** and $[Cp^*Fe(NCPh)_3]^+$

Identification code	**9**	**10**	$[Cp^*Fe(NCPh)_3]^+$
Empirical formula	$C_{29}H_{25}NO_4$	$C_{14.5}H_{12.5}N_{0.5}O_2$	$C_{31}H_{30}F_6FeN_3P$
Formula weight	451.50	225.75	645.40
Temperature/K	170.00(10)	172.99(10)	172.99(10)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	I2/a	$P2_1/n$
a/Å	10.8616(4)	9.4775(2)	15.8364(5)
b/Å	9.2071(4)	10.9889(3)	10.9603(3)
c/Å	24.3258(9)	22.4345(4)	18.9161(6)
α/°	90	90	90
β/°	101.336(4)	92.282(2)	108.912(3)
γ/°	90	90	90
Volume/Å^3	2385.21(17)	2334.64(9)	3106.06(17)
Z	4	8	4
Density (calculated) (g/cm^3)	1.257	1.285	1.380
Absorption coefficient (mm^{-1})	0.673	0.687	4.919
F(000)	952.0	952.0	1328.0
Radiation	Cu*K*α (λ = 1.54184)	Cu*K*α (λ = 1.54184)	CuKα (λ = 1.54184)
Crystal color, morphology	Colorless, block	Colorless, block	Colorless, block
2θ range (°)	7.412 to 155.814	8.962 to 134.086	6.35 to 134.158
Absorption correction	Multi-scan	Multi-scan	Multi-scan
T_{min}, T_{max}	0.805, 1.000	0.267, 1.000	0.249, 1.000
Index ranges	-13 ≤ h ≤ 13, -9 ≤ k ≤ 11, -30 ≤ l ≤ 27	-9 ≤ h ≤ 11, -12 ≤ k ≤ 13, -24 ≤ l ≤ 26	-18 ≤ h ≤ 18, -13 ≤ k ≤ 10, -22 ≤ l ≤ 22
Reflections collected	13755	7248	18035
Independent reflections	4710 [R_{int} = 0.0446, R_{sigma} = 0.0488]	2054 [R_{int} = 0.0310, R_{sigma} = 0.0296]	5473 [R_{int} = 0.0547, R_{sigma} = 0.0518]
Goodness-of-fit on F2	1.051	1.100	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0803, wR_2 = 0.2242	R_1 = 0.0377, wR_2 = 0.0932	R_1 = 0.0493, wR_2 = 0.1312
Final R indexes [all data]	R_1 = 0.0994, wR_2 = 0.2485	R_1 = 0.0456, wR_2 = 0.1040	R_1 = 0.0668, wR_2 = 0.1420
Largest diff. peak/hole / e Å^{-3}	0.69/-0.35	0.24/-0.24	0.68/-0.42

6. References

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